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PREFACE

This volume retains the same framework of basic topics that has been used in the previous five volumes of this series. In order to improve the coverage and to take into account the variations in activity in the various fields of research, there have been some changes made. The establishment of the *Annual Review of Nuclear Science* has given such detailed coverage to work on radioactivity that we have omitted a review of that subject from this issue. It is hoped that from time to time we may include a brief summarizing review of this field for the benefit of those readers who are not interested in the detail contained in the more elaborate review volume. Photochemistry is omitted again as a separate topic but the division of chemical kinetics into two parts which include photochemistry has been continued. Molecular structure and crystallography have been combined in a single review. Spectroscopy has been divided into two parts and the work on microwaves has been included in one part. A completely new topic is presented in the review of chelate compounds.

We wish to express our thanks to all who have contributed to the preparation of this volume. The task of surveying the vast amount of literature in the field of physical chemistry which appears each year would be impossible without the assistance of many scientists. We hope that we will continue to receive excellent cooperation in the future as we have in the past.

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ERRATA

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page 160, reference 57: *for* Alder, G., *read* Alder, M. G.
page 489, lines 29 and 31: *for* 40 *read* 46
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THERMOCHEMISTRY AND THE THERMODYNAMIC PROPERTIES OF SUBSTANCES[1]

By D. W. Scott

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This review concerns a branch of physical chemistry that had its beginning in the period when chemistry emerged as a recognized branch of natural philosophy. In fact, one of the early thermochemists was "the father of chemistry," Antoine Lavoisier, whose calorimetric researches included determinations of the heats of combustion of hydrogen, charcoal, phosphorus, candle wax, and olive oil and the heat of reaction of potassium nitrate with charcoal. Thus, the field of thermochemistry is at least 170 years old. The related field of chemical thermodynamics grew up at its side as the laws of thermodynamics were discovered and consolidated. These fields, despite their age, still attract able investigators with a multitude of challenging problems, as witnessed by the number of research publications in the period covered by this review.

The reason for the continuing, and perhaps increasing, interest in thermochemistry and chemical thermodynamics is not hard to see. The long-range aim is to obtain accurate values of standard heat and free energy of formation of all chemical substances of interest, so that accurate values of standard heat of reaction and equilibrium constant may be calculated for any chemical reactions of interest. When it is remembered that "chemical substances of interest" may include any of the half million or so compounds now known and the hundreds discovered each year, it is seen that the endeavor has just begun. Moreover, if the restriction of "standard" is removed and replaced by "under conditions of interest," the endeavor is compounded manyfold. The accumulation of data on the heat and free energy of formation of chemical substances is not, however, a matter of routine determination, by established methods, of more numbers to fill more pages of tables. On the contrary, the acquisition of such data ever poses new problems to test the abilities of the ablest experimenter, and the interpretation of experimental observations often calls for a high degree of theoretical ingenuity. Furthermore, the coproducts of many thermodynamic studies, such as a clearer insight into the detailed structure and energetics of molecules and crystals, may seem more rewarding than the additions to the store of chemical thermodynamic information that come from the studies. The contributions of thermodynamics to the study of molecular and crystal structure, and indeed to nearly all fields of physical chemistry, are important topics, which, however, are more appropriate to reviews of these other fields and will not be considered here.

[1] This review covers recent publications on thermochemistry and chemical thermodynamics that were not covered by previous reviews of this series and that were available to the reviewer in the original or as abstracts before January 1, 1955.

The number of significant research publications within the scope of this review is so large that even passing mention of each one individually would consume all of the allotted space for this chapter and produce merely a dull, uncritical catalogue of published papers. Alternatively, most of these publications are mentioned only in concise tables that list chemical thermodynamic studies within the scope of this review. Tables I and III list, for inorganic and organic substances, respectively, those substances for which chemical thermodynamic properties were measured or calculated, letter symbols to designate the particular properties measured or calculated, and references to the bibliography at the end of the chapter. The key to the letter symbols for the thermodynamic properties is given in the footnote of each table. Table II lists those studies of inorganic chemical equilibria from which no values of heat or free energy of formation were derived explicitly. (Studies of chemical equilibria that led to values of ΔH_f° or ΔF_f° are included in Table I.) These tables will serve as a basis for the discussion, in the rest of this chapter, of significant trends and important developments. Usually only those publications that are particularly illustrative of these trends or that report particularly significant developments will be singled out for individual mention.

Chemical Thermodynamics of Inorganic Substances

Inspection of Tables I and II will show that chemical thermodynamic studies have dealt with compounds of many elements in the periodic table; 60 elements altogether plus 2 isotopes of common elements. It is almost a truism that the kinds of substances on which chemical thermodynamic studies are most actively pursued reflect activity and new advances in other branches of chemistry in the recent past. Advances in other branches of chemistry open up new fields for thermodynamic investigation and bring new problems for solution by thermodynamic methods. Also, advances in other branches of chemistry often make samples of particular substances of adequate purity for thermodynamic studies available for the first time. The latter is not a trivial consideration, because macroscopic quantities of substances are needed for calorimetric investigations, and the substances must be of high purity if reliable values of chemical thermodynamic properties are to be obtained.

Advances in nuclear science have made available chemical elements that do not occur naturally on this planet, that were unknown a little over a decade ago, and were scarcely dreamed of a few years before that. Availability of these "man-made" elements has opened up whole new fields of study in inorganic and physical chemistry, including chemical thermodynamics. Recent thermodynamic explorations in these fields are the study of the equilibrium in the vapor-phase hydrolysis of americium trichloride (Koch & Cunningham (100)] and several calorimetric studies in the helium isotope of mass 3 in the liquid state [Kerr (92); DeVries & Daunt (33, 34); Osborne, Abraham & Weinstock (134); and Roberts & Sydoriak (142)]. Studies of liquid He^3 are interesting because of the light they may throw on the unusual

and still somewhat baffling properties of the common isotope, He^4, in the liquid state.

The use of ion exchange methods for separating rare earths, which has replaced the older, laborious fractional crystallization methods, has made samples of these elements more readily available than formerly and the designation "rare" somewhat less appropriate. Stimulation of research on the rare earths by the more convenient separation method is reflected in the study of gadolinium metal by low-temperature calorimetry [Griffel, Skochdopole & Spedding (68)], the determination, by solution calorimetry, of the heats of formation of eleven rare-earth trichlorides and hydrated trichlorides [Spedding & Flynn (161, 162)], and studies of the equilibria in the vapor-phase hydrolysis of neodymium trichloride and praseodymium trichloride [Koch & Cunningham (101)].

Current activity in fluorine chemistry is especially evident in recent chemical thermodynamic research; 15 inorganic fluorine compounds are included in Table I. Interest in the metallurgy of some of the minor metals of commerce is seen in thermodynamic studies of compounds of manganese, vanadium, niobium, tantalum, titanium, and zirconium: Mn_2O_3 and Nb_2O_5 [King (96)]; Mn_2O_3 and VO [Orr (133)]; Ta_2O_5, Nb_2O_5, ZrO_2 and TaC [Humphrey (84)]; and $CaTiSiO_5$ [King, Orr & Bonnickson (97)]. Continuing investigation of coordination compounds is reflected in colorimetric studies of isomeric platinum complexes [Chernyaev, Palkin & Sokolov (19)], and equilibrium studies of cobalt carbonyls [Ercoli & Barbieri-Hermitte (47)].

The chemical elements play a particularly important role in chemical thermodynamics. The heat and free-energy changes of chemical reactions are usually calculated as differences in values of heat and free energy of formation of the products and reactants from their constituent elements. Accurate values of the thermodynamic properties of elements are essential if accurate values of heat and free energy of formation are to be calculated for temperatures other than those of direct measurement. It is important that continuing studies be made of the elements as advances in experimental methods make possible more accurate determination of their thermodynamic properties. Table I lists studies of heat capacity or high-temperature enthalpy for 12 elements (the Third-Law entropy was obtained for 5 of these), heat-of-fusion determinations for 2 elements, studies of PVT behavior for 3 elements, vapor pressure determinations for 5 elements, determinations of heats of vaporization or sublimation for 4 elements, and calculations of thermodynamic functions for 2 elements.

Thermodynamic properties of many elements are of interest for reasons other than their use in calculations of heat and free energy of formation. The thermal behavior of *para* hydrogen and helium illustrate the operation of quantum effects at low temperatures. The heavier inert gases are the substances most likely to follow the law of corresponding states, and data of state such as those obtained for xenon by Habgood & Schneider (71) and by Michels, Wassenaar & Louwerse (128) are useful references for determin-

TABLE I

THERMODYNAMIC PROPERTIES MEASURED OR CALCULATED INORGANIC COMPOUNDS

Compound	Property*	Reference	Compound	Property*	Reference
H_2	p	(89)	PCl_3	u	(129)
H_2(*para*)	bl	(159)	Sb	a	(35)
D_2	p	(54)	Bi	a	(90)
H_2O_2	afglm	(64)	CO_2	pqrst	(91, 177)
He	k	(12)	HNCO	qrst	(111)
He^3	blp	(33, 34, 92, 134, 142)	SiO	u	(16)
			SiH_4	qrst	(18)
Xe	p	(71, 128)	SiH_3Cl	qrst	(18)
Cl_2O	qrst	(110)	$SiHCl_3$	qrst	(18)
HOCl	qrst	(110)	$SiCl_4$	qrst	(18)
BrO_3^-	suv	(126)	GeH_3Cl	qrst	(108)
BrCl	qstuv	(124)	GeD_3Cl	qrst	(108)
IF_5	fik	(143)	Sn	abij	(10, 152)
S	b	(15)	SnO	hj	(160)
S_8	qrstuv	(70)	Pb	abgnqrst	(10, 38)
$S_2O_3^-$	suv	(126)	PbI^+	suv	(178)
SF_6	qst	(59)	InS	v	(171)
S_2Cl_2	qrst	(112)	In_2S_3	v	(171)
$SOCl_2$	u	(129)	In_3S_4	v	(171)
SO_2Cl_2	u	(129)	In_2S_3	v	(171)
SeF_6	qst	(59)	TlN_3	u	(117)
TeF_6	qst	(59)	Zn	hj	(118)
N_2	i	(6)	$HZnO_2^-$	v	(55)
NH_4NO_3	lnv	(50)	$ZnO_2^=$	v	(55)
Cd	al	(26)	BH_3CO	qrst	(58)
CdO	uv	(119)	$Al(OH)_4^-$	v	(105)
CdI^+	suv	(178)	AlF_3	u	(69)
HgI^+	suv	(178)	Gd	adlqrs	(68)
$HgINO_3$	u	(178)	YCl_3	uv	(161, 162)
Ag	h	(113)	$YCl_3 \cdot 6H_2O$	uv	(161, 162)
$Ag_3I(NO_3)_2$	u	(178)	$ErCl_3$	uv	(161, 162)
Pt_3O_4	u	(5)	$ErCl_3 \cdot 6H_2O$	uv	(161, 162)
ReF_6	qst	(60)	$GdCl_3$	uv	(161, 162)
NiO	uv	(14)	$GdCl_3 \cdot 6H_2O$	uv	(161, 162)
NiF_2	ad	(167)	$PrCl_3$	uv	(161, 162)
Ni_3S_2	uv	(144)	$PrCl_3 \cdot 6H_2O$	uv	(161, 162)
Ni_6S_5	uv	(144)	$PrCl_3 \cdot 7H_2O$	uv	(161, 162)
NiS	uv	(144)	$LaCl_3$	uv	(161, 162)
NiS_2	uv	(144)	$LaCl_3 \cdot 7H_2O$	uv	(161, 162)
CoO	uv	(14)	U	ik	(141)
CoF_2	ad	(167)	UF_6	qst	(59)
Co_4S_3	uv	(144)	ThO_2	hj	(76)
Co_9S_8	uv	(144)	ThF_4	alqrst	(107)

TABLE I (Continued)

Compound	Property*	Reference	Compound	Property*	Reference
CoS	uv	(144)	ThI_2	uv	(3)
FeF_2	ad	(167)	BeF_2	jl	(153)
FeS	uv	(144)	Mg	al	(26)
FeS_2	uv	(144)	MgO	h	(17)
Mn_2O_3	aln	(96, 133)	$Mg_3P_2O_8$	u	(166)
MnS	u	(87)	Mg_3Cd	al	(23)
$Mn_3P_2O_8$	u	(166)	MgCd	al	(148)
Mn_2SiO_4	u	(87)	$MgCd_3$	al	(23)
Cr_3C_2	nqrs	(132)	$MgFe_2O_4$	adeln	(13, 95)
Cr_2O_3	uv	(119)	$CaFe_2O_4$	afgln	(13, 95)
MoF_6	qst	(59)	$Ca_2Fe_2O_5$	afgln	(13, 95)
MoI_2	uv	(3)	$CaTiSiO_5$	afgln	(97)
$MoSi_2$	nrst	(41)	Li	n	(11)
WF_6	qst	(59)	LiF	fgnqrst	(39)
VO	n	(133)	Na	a	(29)
Nb_2O_5	aluv	(84, 96)	NaOH	defgnqrst	(37)
Ta_2O_5	uv	(84)	NaOH(aq)	u	(93)
TaC	uv	(84)	KOH(aq)	u	(93)
Ti	qrst	(103)	KCl	hj	(173)
TiO_2	a	(43)	RbCl	hj	(173)
ZrO_2	hjuv	(77, 84)	Cs	fg	(21)
ZrF_4	h	(154)	CsCl	hj	(173)
BN	aloqrstuv	(44)			

* Key to letter symbols for thermodynamic properties:

a	C_p or C_{satd} of solid	l	Entropy of solid or liquid
b	C_p or C_{satd} of liquid	m	Entropy of gas
c	C_p of gas	n	High temperature enthalpy
d	Transition temperature	o	Heat of combustion
e	Heat of transition	p	Data of state
f	Triple point	q	$F°-H_0°$ or $(F°-H_0°)/T$
g	Heat of fusion	r	$H°-H_0°$ or $(H°-H_0°)/T$
h	Vapor pressure of solid	s	$S°$
i	Vapor pressure of liquid	t	$C_p°$
j	Heat of sublimation	u	$\Delta H_f°$
k	Heat of vaporization	v	$\Delta F_f°$

ing how much other substances deviate from corresponding states behavior. The molecular complexity of sulfur in the liquid and vapor states is still not thoroughly understood, and thermodynamic studies such as Braune & Möller's measurements of heat capacity for the liquid (15) will aid in the eventual understanding of this element's complex behavior. Thermodynamic data for the metallic elements have applications in the theory of metals.

Chemical thermodynamic research tends to push into those areas which have recently been opened by advances in other branches of chemistry. This

TABLE II

CHEMICAL EQUILIBRIA STUDIED, INORGANIC

Equation	Reference
$SO_2=SO+1/2O_2$; $1/2S_2+1/2O_2=SO$	(168)
$Hg+Hg^{++}=Hg^{+}$	(151)
$Cu_2Te=2Cu+Te_2$	(102)
$Cu_2S+H_2=2Cu+H_2S$	(94)
$1/3MWO_4+H_2=1/3MO+1/3W+H_2O$(M = Ca, Mg, & Mn)	(63)
$1/4MWO_4+H_2=1/28M_7W_6+1/28W+H_2O$(M = Fe & Co)	(63)
$1/4NiWO_4+H_2=1/16Ni_4W+3/16W+H_2O$	(63)
$CaMoO_4+H_2=CaMoO_3+H_2O$	(63)
$1/2CaMoO_3+H_2=1/2CaO+1/2Mo+H_2O$	(63)
$CoCl_2+H_2=Co+2HCl$	(147)
$2[Co(CO)_4]_2=[Co(CO)_3]_4+4CO$	(47)
$NiCl_2+H_2=Ni+2HCl$	(147)
$FeS_2+H_2=FeS+H_2S$	(86)
$2FeS_2=2FeS+S_2$	(86)
$AlI_3+3HCl=AlCl_3+3HI$	(24)
$NdCl_2+H_2O=NdOCl+2HCl$	(101)
$PrCl_3+H_2O=PrOCl+2HCl$	(101)
$AmCl_3+H_2O=AmOCl+2HCl$	(100)
$ThO(OH)_2+2H^{+}=ThO^{++}+2H_2O$ and related equilibria	(61)

fact, and the fact that the accuracy of thermodynamic measurements has improved over the years, often leads to the situation that chemical thermodynamic data for uncommon or newly discovered substances have been determined recently by highly accurate methods, whereas similar data for common, long-known substances were determined years ago by much less accurate methods. Such a situation cannot persist indefinitely. The needs of advancing science and technology for better thermodynamic data for common, and often commercially important, substances, or for data over a wider range of conditions, require eventual reinvestigation of these common substances. It is not surprising, therefore, to find in Table I such old friends from the days of the high school "chem lab" as sodium hydroxide and ammonium nitrate [Douglas & Dever (37); Ketchen & Wallace (93); and Feick (50)].

One investigation which deserves special mention because of the difficult experimental problems that were overcome is determination of the entropy of hydrogen peroxide by low temperature calorimetry [Giguere *et al.* (64)]. In order not to expose the sample to surfaces that would catalyze its decomposition, these workers used all-aluminum calorimeters, the joints of which were arc welded, including the final seals after the samples had been introduced. The interior surfaces were given extensive passivation treatment. Giguere and his co-workers were able to prepare and maintain in the calorimeters a sample of hydrogen peroxide of better than 99.96 mole per cent

purity. Third-law studies of hydrogen peroxide have been considered by workers in the field for many years, but no one heretofore had the audacity to undertake work with this difficult-to-purify and unstable substance.

Activity in high-temperature chemistry is reflected in some of the investigations summarized in Table I. Most of the chemical thermodynamic studies at high temperatures have been determinations of vapor pressure and heats of sublimation and vaporization of metals and compounds which exist at ordinary temperatures. However, the determination by Brewer & Edwards (16) of the heat of formation of silicon monoxide (SiO) is an example of a chemical thermodynamic study of a substance which does not exist at ordinary temperatures in a form suitable for study. Advances in high-temperature chemistry may be expected to lead to an increasing number of chemical thermodynamic investigations of substances that the investigator cannot keep in a bottle on his laboratory bench.

The evaluation and correlation of thermodynamic data are important aspects of chemical thermodynamics, especially when results by different methods or from different investigations must be used for the critical selection of values for a substance. Shomate (155) has proposed a sensitive method for treating high-temperature enthalpy data when a value of the heat capacity at 298.16°K. is known. The function

$$\frac{T(H_T - H_{298.16}) - C_{p298.16}(T - 298.16)]}{(T - 298.16)^2}$$

is plotted against Kelvin temperature. Shomate gives examples of the use of such a plot for smoothing high-temperature enthalpy data, evaluating heats of transition and fusion, and calculating values of high-temperature heat capacity. In favorable instances, the method may also be used to get algebraic expressions for the heat capacity and enthalpy or to extrapolate to temperatures higher than those of the experimental measurements.

Dissociation energy and heat of atomization.—Heat and free energy of formation values are based on those forms of the elements most stable or most common at room temperature and one atmosphere pressure. If, instead, the standard states of the elements could be selected as the free gaseous atoms, values of heat and free energy of formation would have greater theoretical significance. Unfortunately, even for some of the common elements, such a choice of standard states cannot be made at this time because the heats of formation of the gaseous atoms from the forms stable at room temperature and one atmosphere pressure are not known. The more important values still in doubt are the heats of dissociation of N_2, F_2 and S_2 and the heat of sublimation of carbon (graphite). For N_2, S_2 or graphite, the choice is between two or three values known from spectroscopic studies, but the decisions as to which of the two or three is the correct one have proved to be among the most baffling and exasperating problems of present-day thermochemistry.

A reviewer would like to be able to report that at least one of these problems has been settled to everyone's satisfaction, but, unfortunately, that

cannot be done. Instead, it is necessary to summarize another year's collection of conflicting experimental evidence and theoretical speculation which must be reconciled before any of these problems can be settled.

Hendrie (75) was unable to detect nitrogen atoms in a molecular beam effusing from a furnace that contained nitrogen gas and concluded that his observations established a lower limit of about 200 kcal. mole^{-1} for the dissociation energy of N_2. Such a lower limit would exclude the lower proposed value (170 kcal. mole^{-1}) in favor of the higher one (225 kcal. mole^{-1}). Pauling (137), from considerations of the dependence of bond energy on bond length, favored the 170 kcal. mole^{-1} value.

Wise (176) measured the heat of dissociation of F_2 by an effusion method and obtained a value of 37.6 kcal. mole^{-1}. Sanderson (146) pointed out that a value as low as 37 kcal. mole^{-1} is out of line with the other halogens when dissociation energy is plotted against other properties.

St. Pierre & Chipman (168), from studies of the composition of lime-iron oxide slags in equilibrium with SO_2 or SO_2-CO mixtures, favored the intermediate value (83 kcal. mole^{-1}) for the heat of dissociation of S_2 [and the high value (118.7 kcal. mole^{-1}) for the heat of dissociation of SO].

The problem of the heat of sublimation of graphite received much attention. Doehaerd, Goldfinger & Waelbroeck (36, 66) interpreted the results of their effusion experiments to indicate that carbon has a low accommodation coefficient and report the value 141.7 kcal. mole^{-1} for the heat of sublimation. Langer, Hipple & Stevenson (106), from results of electron impact studies with methane, favored a value of about 136 kcal. mole^{-1} for the heat of sublimation of graphite to monoatomic carbon. Pauling (137), from considerations similar to those for N_2, favored the low value of about 139 kcal. mole^{-1}. Chupka & Ingram (20) and Honig (78) used mass-spectrometer methods to observe the carbon vapor emitted from a Knudsen cell and from heated filaments, respectively. Neutral species, C_1, C_2, C_3, and C_5 and negative ions up to C_8^- were observed. The experimental results were interpreted to favor the high value of about 170 kcal. mole^{-1} for sublimation to monoatomic carbon. Other evidence for the molecular complexity of gaseous group IV elements came from the work of Honig (79, 80), who studied the vapors from evaporating germanium and silicon and found neutral species up to Ge_4 and Si_7. Glockler (65) made thermodynamic calculations for carbon vapor assumed to consist only of the three species C_1, C_2, and C_3 and found that the calculations were consistent only with the high value of about 170 kcal. mole^{-1} for the heat of sublimation of graphite to C_1. Although the heat of sublimation of graphite is still a matter of controversy, one fact emerges clearly from these studies. Carbon and the higher group IV elements must be included, along with phosphorus, sulfur, and the higher group V and group VI elements, in the class of elements that exist in the vapor state as a complex mixture of molecular species.

Chemical Thermodynamics of Organic Substances

Inspection of Table III will show that thermodynamic studies have been

made for a great variety of organic substances—hydrocarbons, oxygen compounds, nitrogen compounds, halogen compounds, sulfur compounds, organoboron and organosilicon compounds, and metal-organic compounds. The current activity in the field of fluorine chemistry is as apparent in the recent chemical thermodynamic studies of organic substances as it is in those of inorganic substances. Fourteen organic fluorine compounds are listed in Table III; six are completely fluorinated compounds.

Just as the elements are basic to the chemical thermodynamics of inorganic substances, so are the hydrocarbons basic to the chemical thermodynamics of organic substances. The time is not far distant when semiempirical incremental methods can be used to estimate the thermodynamic properties of higher members of whole families of organic compounds with moderate accuracy. These incremental methods require values of the thermodynamic properties of the parent hydrocarbons. It is evident that values of thermodynamic properties estimated by incremental methods can never be any more reliable than the values for the parent hydrocarbons that are used in the incremental calculations.

The accumulation, mostly within the last 15 years, of a large body of reliable thermodynamic information for hydrocarbons is one of the highlights of recent thermodynamic research in the organic field. Nevertheless, this body of thermodynamic information for hydrocarbons must be expanded and kept up-to-date by more accurate experimental determinations if the chemical thermodynamics for all organic substances is to rest on a firm foundation. Illustrative of recent additions to data for hydrocarbons are the determinations of Finke and co-workers (51), by low-temperature calorimetry, of the entropy of the nine liquid *n*-paraffin hydrocarbons, octane through hexadecane, inclusive. Experimental determinations have now been made of the entropy of all liquid *n*-paraffins through $C_{16}H_{34}$, and reliable extrapolations are possible for the next few higher members of the series.

The dependence of progress in chemical thermodynamics on the availability of carefully purified samples of compounds for use in calorimetric studies has already been mentioned. Certainly, the rapid advances in the chemical thermodynamics of hydrocarbons are owing, in part, to the availability of samples of known high purity through American Petroleum Institute Research Projects 6 and 44. More recently, A.P.I. Research Project 48 has been preparing samples of highly purified sulfur compounds, portions of which are used for calorimetric studies. Thermodynamic studies of 10 hydrocarbons and 7 sulfur compounds included in Table III were made with A.P.I. samples. The recently established A.P.I. Research Project 52 has as one of its functions the preparation of highly purified samples of nitrogen compounds, portions of which are also to be used for calorimetric studies.

The body of chemical thermodynamic data for inorganic substances has been accumulated at a rather steady rate since the development of chemical thermodynamics as a recognized branch of physical chemistry in the early years of this century. The body of chemical thermodynamic data for organic substances, on the other hand, has been obtained at an accelerating rate

TABLE III

THERMODYNAMIC PROPERTIES MEASURED OR CALCULATED
ORGANIC COMPOUNDS

Compound	Property*	Reference
Ethane	p	(127)
Isopentane	p	(85)
n-Heptane	abfgnqrst	(40)
n-Paraffins, octane to hexadecane, incl.	abdefgl	(51)
n-Paraffins	qrst	(172)
Two polybutadienes	a	(56)
Ketene	q	(9)
Cycloöctatetraene	o	(164)
α- and β-Pinene	i	(73)
α- and β-Pinene, dipentene, *d*-limonene *cis*-alloöcimene, and myrcene	o	(74)
Perdeuterobenzene and perdeuterocyclohexane	ik	(30)
Methanol, ethanol, and isopropanol	p	(104)
Methanol, propanol, isopropanal, and butanol	p	(62)
Propanol, butanol, and ethylene glycol	qrs	(46)
Acetone and ketene	qrst	(99)
Five-carbon fatty acids and their methyl and ethyl esters	ou	(72)
d- and *dl*-Dimethyltartrate	hijk	(27)
Diacetyl, benzil, benzylmethylketone, and dibenzylketone	ikou	(163)
Diacetyl and benzylmethylketone	ikou	(130)
Acetic acid and perdeutero-acetic acid	i	(140)
Butyl α-hydroxyisobutyrate and dibutyl ether	i	(53)
Benzoic, salicylic, *p*-hydroxybenzoic, and *o*-methoxybenzoic acids	hj	(32)
d-Camphor and *dl*-camphor	adeh	(149)
Formamide	qrst	(48)
Ethyl nitrate	abfglv	(67)
Unsymmetrical dimethyl hydrazine	abfgikl	(8)
Nitromethane	cikpqrstuv	(116)
Pyridine, α-, β-, and γ-picoline, and 2,5- and 2,6-lutidine	ou	(25)
Cyclopentylazide and cyclohexylazide	ou	(49)
Perfluoropropane	c	(123)
Octafluorocyclobutane	abdefgiklm	(57)
CF_3CHCl_2 and CF_3CCl_3	qrst	(109)
$CF_2=CF_2$ and $CCl_2=CCl_2$	qrst	(121)
CCl_4 and n-C_7F_{16}	p	(2)
CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, C_2F_6, CF_2ClCF_2Cl, C_2F_4 and $CF_2=CFCl$	u	(98)
CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, and CCl_4	qrst	(1)
CH_4, CH_3Cl, $CHCl_3$, and CCl_4	qrst	(18)
Cis- and *trans*- $CHCl=CHCl$	qrst	(139)
CH_3CH_2Cl and CH_3CHCl_2	qrst	(28)
CCl_3CH_2Cl and CCl_3CHCl_2	qrst	(131)

TABLE III (Continued)

Chlorobenzene, *o*-, *m*-, and *p*-dichlorobenzene, *o*- and *p*-chloroethylbenzene	ou	(82)
o-Dichlorobenzene	in	(174)
Hexachlorocyclohexane	o	(150)
Trichloroacetonitrile	ikqrst	(31)
CH_2Br_2, CD_2Br_2, and $CHDBr_2$	qrst	(42)
CH_2I_2	qrst	(175)
2-Propanethiol	abcdefgikl pqrstuv	(115)
Thiacyclohexane	abcdefgklmo qrstuv	(114)
1-Pentanethiol, 3-thiapentane, 2-methyl-2-propanethiol, thiacyclopentane, thiacyclobutane, and thianthrene	ou	(81)
Thianthrene	o	(169)
Benzothiophene	abdefgl	(52)
N-Dimethylaminodiborane	qrst	(120)
Ethoxydichloroborine and diethoxychloroborine	u	(158)
Dimethylaminodichloroborine, bisdimethylaminochloroborine, and trisdimethylaminoborine	u	(156, 157)
Octamethylcyclotetrasiloxane	fik	(135)
Some methoxypolysilanes and methoxypolysiloxanes	ou	(170)
Twenty organosilicon compounds	i	(88)
$(CH_3)_4Sn$, $(CH_3)_4Pb$, $(C_2H_5)_4C$, $(C_2H_5)_4Si$, $(C_2H_5)_4Ge$, $(C_2H_5)_4Sn$, and $(C_2H_5)_4Pb$	abfg	(165)

[a] Key to letter symbols for thermodynamic properties:

a	C_p or C_{satd} of solid	l	Entropy of solid or liquid
b	C_p or C_{satd} of liquid	m	Entropy of gas
c	C_p or gas	n	High temperature enthalpy
d	Transition temperature	o	Heat of combustion
e	Heat of transition	p	Data of state
f	Triple point	q	$F°-H_0°$ or $(F°-H_0°)/T$
g	Heat of fusion	r	$H°-H_0°$ or $(H°-H_0°)/T$
h	Vapor pressure of solid	s	$S°$
i	Vapor pressure of liquid	t	$C_p°$
j	Heat of sublimation	u	$\Delta H_f°$
k	Heat of vaporization	v	$\Delta F_f°$

mostly within the past 15 or 20 years. In 1932 Parks & Huffman could summarize most chemical thermodynamic knowledge for organic substances between the covers of a monograph of 243 pages (136). By 1953, when the latest issue of the A.P.I. Research Project 44 tables (145) was published, over 450 pages were required for tables of chemical thermodynamic information for hydrocarbons alone. It is doubtful if the existing data for all organic compounds could possibly be contained in a single volume. Of the factors which have contributed to this accelerating development of chemical thermodynamics for organic compounds, three are particularly noteworthy: (*a*) The

use of low-temperature calorimetry to determine entropies of organic compounds by application of the Third Law; (*b*) the use of the methods of statistical mechanics to compute thermodynamic functions for organic compounds from spectroscopic and molecular structure information; and (*c*) the use of precision reaction calorimetry to determine heats of formation of organic compounds. These three factors, and current trends and significant developments relative to them, will be discussed in turn.

Low-temperature calorimetry.—As low-temperature calorimetry for organic and inorganic substances differs only in the kind of sample put into the calorimeter, much of what is said here about low-temperature calorimetry applies to both classes of substances. The experimental methods of low-temperature calorimetry have become reasonably well standardized, but there is interest in improving the speed and convenience with which experimental results may be obtained, in particular by use of automatic instrumentation. Dauphinee, MacDonald, & Preston-Thomas (29) have described a calorimeter of the continuous-heating type for which control of the adiabatic shields around the calorimeter and recording of the data require only occasional attention from the operator. It was designed primarily for studies of alkali metals. Such a calorimeter is best adapted to the study of solids and liquids which attain thermal equilibrium rapidly. Continuous-heating type calorimeters are not suitable for studies in regions of anomalous heat capacity and near transitions and melting points where attainment of thermal equilibrium usually is slow. Automatic controls versatile enough to maintain adiabatic conditions for the more conventional intermittent-heating type calorimeters have not yet been developed, but the rapid strides that are being made in automatic instrumentation make such a development a distinct possibility.

One of the best methods of checking the reliability of physical measurements and seeking for undetected sources of systematic error is the intercomparison of results obtained in different laboratories with identical samples. Such an intercomparison for low-temperature calorimetry (and also high-temperature enthalpy studies) was recommended by the Fourth Calorimetry Conference in 1949. Following this recommendation, the National Bureau of Standards prepared and packaged samples (for intercomparison of heat-capacity measurements) of *n*-heptane, synthetic sapphire, and benzoic acid for distribution to qualified investigators by the Calorimetry Conference. Recently, Douglas *et al.* (40) have reported results of low-temperature calorimetric studies made at the National Bureau of Standards with the *n*-heptane sample. Similar studies by several, and preferably most, laboratories engaged in low-temperature calorimetry will be necessary before the intercomparisons can be used to assess the reliability of present methods of low-temperature calorimetry.

An interesting by-product of low-temperature calorimetry is the frequent discovery of solid-state transitions, lambda points, and other kinds of anomalous thermal behavior, and of polymorphism. The observance of such

phenomena has become almost commonplace as more complex substances, both organic and inorganic, are being studied. Substances which exist in a single crystalline form with regular heat-capacity behavior over the entire temperature range from 0°K. to the melting point now seem to be the exception rather than the rule. (The observance of solid-state transitions is also a frequent occurrence in high-temperature enthalpy studies.) The publications covered by this review have reported more such phenomena than may feasibly be mentioned individually. Particularly striking examples are the four isothermal transitions in octafluorocyclobutane, two of which are only 2° apart [Furukawa, McCoskey & Reilly (57)], the prominent lambda-type anomaly in benzothiophene, presumably an order-disorder transition [Finke *et al.* (52)], and the 10 polymorphic forms of tetraethyltin and the 8 polymorphic forms of tetraethyllead [Staveley *et al.* (165)]. Calorimetric studies are a powerful tool for discovering such phenomena, measuring the temperatures at which they occur and the associated energy effects, finding the conditions for existence of metastable crystalline forms, and observing whether transitions are rapid or sluggish. However, calorimetric studies are usually of little value in explaining the detailed mechanism of such phenomena at the molecular level. Detailed understanding will have to come from determinations of crystal structure by X-ray diffraction, nuclear magnetic resonance studies, measurement of dielectric constants, and perhaps other methods not yet developed. Workers in the appropriate branches of solid-state physics will find the literature of low-temperature calorimetry a rich source of fascinating problems for their attention.

Thermodynamic functions by methods of statistical mechanics.—The calculation of thermodynamic functions from spectroscopic and molecular structure data has attracted the attention of many investigators. The publications covered by this review report calculations of thermodynamic functions in the ideal gas state for 22 inorganic and 33 organic substances. (See Tables I & III.) Many of the calculations are reported by spectroscopists who wish to derive the maximum of useful information from the results of their spectroscopic researches. The recent tendency to include calculated values of thermodynamic functions in reports of spectroscopic investigations is a gratifying one. Contributions to the body of chemical thermodynamic information by investigators whose primary interest is not thermodynamics are highly welcome.

The use of the methods of statistical mechanics, which started in the 1920's and was first applied to simple monoatomic and diatomic gases, has depended on the availability of the kinds of data needed for the calculation of thermodynamic functions. These needs have been met by the discovery of Raman spectra and the use of Raman spectroscopy to determine the fundamental vibration frequencies of many molecules, the development of electron diffraction methods to measure the values of bond distances and angles which are needed to calculate moments of inertia of molecules, and the more recently developed methods of microwave spectroscopy from which values

of moments of inertia are obtained directly. However, the most striking recent development has been the renaissance of the companion study to Raman spectroscopy—the long-known and long neglected study of infrared spectra. Ten or fifteen years ago the person who wished to have infrared spectroscopic data for the calculation of thermodynamic functions might find that Coblentz (22) had studied the compound some time before 1905 or that more recent work with poor resolution and of doubtful reliability was reported in an obscure journal, but usually he was just out of luck. Now, if he can not find the needed spectrum among the 1638 in the A.P.I. catalog (4) or in other collections of infrared data (some on punch cards for mechanical sorting), the determination of the needed data may be a matter of only a few hours with one of the infrared spectrometers that are standard equipment in all larger laboratories. Although the main incentive to the recent advances in infrared spectroscopy was its value for rapid analyses of complex mixtures, mostly in industrial applications, these advances have been an adventitious benefit to chemical thermodynamics. A particularly valuable development from the standpoint of thermodynamics is the extension of infrared measurements to longer wave lengths, i.e., lower frequencies. Since low-frequency molecular vibrations make greater contributions to the thermodynamic functions than high ones, it is especially important that the low frequencies be observed and correctly assigned. A few years ago infrared spectroscopy was practically limited to studies in the rocksalt region (frequencies above about 670 $cm.^{-1}$). Now the use of potassium bromide optics (400 to 670 $cm.^{-1}$) is almost commonplace, and the use of KRS5 optics (250 to 400 $cm.^{-1}$) is no longer rare. Among the publications covered by this review which include calculated values of thermodynamic functions, 11 also report infrared measurements in the potassium bromide region, and 4 report infrared measurements in the KRS5 region. Other reported calculations of thermodynamic functions utilized literature data for these regions of the infrared spectrum. Infrared studies have been extended to even lower frequencies with grating spectrometers. Pitzer & Hollenberg (139) obtained the infrared spectra of *cis-* and *trans-* dichloroethylene between 140 and 300 $cm.^{-1}$ with such a spectrometer and observed directly two fundamental frequencies of the *trans* isomer for which incorrect values had previously been proposed.

Calculations of thermodynamic functions are now made with confidence for substances which as little as five years ago would have been considered hopelessly complex. The application of the methods of statistical mechanics to substances of greater molecular complexity is possible because of the accumulated background of experience with simpler substances and the observation of regularities in vibrational frequencies, barriers to internal rotation, and other details of molecular structure. The successful treatment of one substance is the stepping stone to the treatment of several structurally-related but somewhat more complex substances, the treatment of each of these is the stepping stone to the treatment of other related but still more complex substances, and so outward in ever branching paths.

The interpretation of spectra and the obtaining of complete and reliable vibrational assignments is an important part of the calculation of thermodynamic functions. A valuable aid in the interpretation of spectra is the calculation of vibrational frequencies from force constants and molecular geometry —the so-called "normal coordinate calculations." However, the numerical complexities of normal coordinate calculations are rather formidable. Their use has been limited to rigorous calculations for simple or highly symmetrical molecules or to approximate over-simplified calculations for more complex ones. Mann *et al.* (122) have reported the use of high-speed digital computers for such molecular-vibration calculations. This development promises to make calculations possible that would be out of reason with ordinary desk calculators, and more reliance on normal coordinate calculations may be expected in the future.

Most calculations of thermodynamic functions involve the harmonic-oscillator, rigid rotator approximation, i.e., the small effects of vibrational anharmonicity, rotation-vibration interaction, centrifugal stretching, and the like are neglected. It is recognized that neglect of these effects, of which anharmonicity is usually the most important, introduces small but significant errors into the calculated thermodynamic functions. However, the numerous anharmonicity coefficients and other parameters needed to treat these effects are usually not known, and their determination by spectroscopic methods for complex molecules presents formidable difficulties. McCullough, *et al.* (114) have proposed a semiempirical method for handling the contributions of anharmonicity to thermodynamic functions. The method is quite simple when Pennington & Kobe's tables (138) are used to evaluate the necessary functions. The method requires that two empirical parameters be evaluated from experimental values of the vapor heat capacity, C°_p, at two or more temperatures. This matter of anharmonicity illustrates the fact that the real foundation of chemical thermodynamics is still accurate calorimetry no matter how many values of thermodynamic properties may be calculated from information obtained in other fields. When the contributions of anharmonicity are known for enough substances, it may be possible to generalize and make predictions for substances for which no experimental data exist. Albright, Galegar & Innes's estimates of the anharmonicity contributions for the chlorofluoromethanes (1) are a step in this direction.

Precision reaction calorimetry.—Values of entropy obtained by low temperature calorimetry may be used in the relation, $\Delta F^\circ_f = \Delta H^\circ_f - T\Delta S^\circ_f$, to obtain values of standard free energy of formation. Similarly values of the functions $(F^\circ - H^\circ_0)$ and $(H^\circ - H^\circ_0)$ calculated by methods of statistical mechanics may be used in the relations, $\Delta F^\circ_f = \Delta(F^\circ - H^\circ_0)_f + \Delta H^\circ_{0f}$ and $\Delta H^\circ_f = \Delta(H^\circ - H^\circ_0)_f + \Delta H^\circ_{0f}$, to obtain values of standard free energy and heat of formation as a function of temperature. However, values of the terms ΔH°_f or ΔH°_{0f} are also needed. For organic substances, these must usually be obtained by reaction calorimetry, although in isolated instances they may also be obtained by study of chemical equilibria. Reaction calorim-

etry, therefore, is of fundamental importance in the chemical thermodynamics of organic substances.

For certain classes of organic substances, reaction calorimetry has lagged behind other methods of obtaining chemical thermodynamic information. For many substances, values of entropy have been determined or thermodynamic functions have been calculated, but the heat, free energy, and equilibrium constant for reactions in which these substances participate cannot be calculated because the needed values of ΔH°_f or ΔH°_{0f} are lacking. For other substances, values of ΔH°_f determined back in the nineteenth century are used because no values determined by more accurate present-day methods exist.

One reason for the lag in reaction calorimetry is the much greater diversity of experimental problems. In low temperature calorimetry and molecular spectroscopy, the experimental problems depend very little on the chemical nature of the sample put into the calorimeter or spectrometer, unless special problems are raised by corrosive, reactive, or unstable materials. In reaction calorimetry, on the other hand, the study of each particular class of compounds, and sometimes even an individual member within a class, raises a host of new chemical problems—how to make the reaction proceed cleanly to a well-defined final state, how to detect side-reactions, if any, how to determine the extent of reaction, and other problems specific to the particular reaction. Another reason for the lag in reaction calorimetry is the requirement of extremely high accuracy. The terms, $T\Delta S^\circ_f$ and $\Delta(F^\circ - H^\circ_0)_f$, are commonly known within a few hundred cal. mole^{-1}. Heats of reaction, which may exceed a million cal. mole^{-1}, must be determined with an experimental uncertainty that is very small, often only a few hundredths of a per cent, if the accuracy with which ΔF°_f is known is not limited solely by the accuracy with which ΔH°_f or ΔH°_{0f} is known. The lag in reaction calorimetry is recognized by workers in the field, and serious efforts are being made to increase the output of needed thermochemical data.

Several types of reaction calorimetry are useful in the thermochemical study of organic compounds. The use of solution calorimetry is illustrated by the studies of Skinner & Smith (156, 157, 158) and of Dworkin & Van Artsdalen (45) with organoboron compounds. Kirkbride & Davidson (98) studied the reactions of eight fully fluorinated (or fluorinated and chlorinated) compounds with potassium metal in a calorimeter specially designed for that purpose. Flow calorimetry and flame calorimetry have a place in the overall picture, although no examples of their use appear in the publications covered by this review. However, the type of calorimetry that has shown the greatest versatility in the past and has contributed most to the existing thermochemical data for organic compounds is combustion-bomb calorimetry.

Modern precision combustion-bomb calorimetry dates from the early 1930's. It was initially limited to studies of compounds which contain only

carbon, hydrogen, oxygen, and nitrogen; and it continues to be a fruitful source of thermochemical data for such substances. Seven publications that report heat-of-combustion data for over twenty hydrocarbons, oxygen compounds, and nitrogen compounds are referred to in Table III. Attempts to adapt the standard methods of combustion-bomb calorimetry to halogen compounds, sulfur compounds, and metal-organic compounds have been disappointing, although much thermochemical data of at least moderate accuracy have come from such attempts. The main obstacle was the failure of combustion reactions for such substances to reach well-defined, equilibrium final states in a stationary bomb. This obstacle has now been surmounted by the development, initially in Sweden and more recently in the United States, of moving bomb methods that permit the contents of the bomb to be agitated after the combustion reaction is complete by shaking, rocking, or rotating the bomb. A rotating-bomb method, primarily for the combustion calorimetry of sulfur compounds, has been described by Hubbard, Katz & Waddington (81). Rotating-bomb methods make combustion-bomb calorimetry possible for whole classes of organic compounds for which accurate thermochemical data are rare or completely lacking.

Other aspects of combustion calorimetry that have received attention are (*a*) the corrections to standard states (Washburn corrections), which have been revised and extended to include organic sulfur compounds by Hubbard *et al.* (83), and (*b*) a secondary standard for the combustion calorimetry of sulfur compounds, for which Sunner & Lundin (169) have proposed thianthrene.

Vapor heat capacity measurements; studies of equilibria.—The use of vapor heat capacity data to estimate contributions of anharmonicity was discussed in a previous subsection. The next section will touch upon the application of vapor heat capacity data in the study of gas imperfection and determination of virial coefficients. In addition to these two applications, vapor heat capacity data are also useful, preferably but not always necessarily along with a calorimetric value of entropy, for estimation of unobserved vibrational frequencies, determination of the height of barriers restricting internal rotation, and the study of equilibria between tautomeric forms such as the "chair" and "boat" tautomers of six-membered rings. Examples of these uses of vapor heat capacity data are found in the studies of 2-propanethiol and thiacyclohexane by McCullough, *et al.* (114, 115). Vapor heat capacity studies are such a versatile and powerful tool in thermodynamic investigations that it seems unfortunate that such studies receive as little attention as they do. Vapor heat capacity data from only two laboratories are reported in the publications covered by this review.

Direct studies of chemical equilibria are seldom possible for organic reactions. However, when possible, studies like those of Maury, Burwell & Tuxworth (125) for the equilibria 2-methylhexane = 3-methylhexane and 2,3-dimethylpentane = 2,4-dimethylpentane, and of Aston, Hu & Gittler (7)

of the equilibrium, $CH_3NH_3Cl = CH_3NH_2 + HCl$ (from cell measurements), give accurate values of the free-energy changes and serve as a valuable check on free energy data obtained by the more generally applicable methods.

Data of State

Most of the foregoing discussion has been concerned with thermodynamic properties for substances in their standard states, i.e., solids and liquids under one atmosphere pressure and gases in the ideal gas state at one atmosphere pressure. Thermodynamic calculations for conditions other than the standard states require a knowledge of the pressure-volume-temperature relationships of the substances under consideration. The numerous recent publications on theoretical aspects of PVT behavior are beyond the scope of this review, but a few of the experimental PVT studies listed in the tables will be mentioned here. Studies of xenon have already been mentioned. Isaac, Li & Canjar (85) have studied the volumetric behavior of isopentane at pressures up to 210 atm. and temperatures up to 300°C. Accurate data of state have now been obtained for all of the saturated hydrocarbons up to and including the isomeric pentanes. McCullough, *et al.* (116) have determined the second virial coefficient of nitromethane from measurements of heat of vaporization, vapor pressure, and vapor heat capacity. The second virial coefficient is large, as would be expected for such a polar substance, but third or higher virial coefficients are unimportant at pressures below one atmosphere. Kretschmer & Wiebe (104) have made painstaking determinations of the PVT relationships of methyl, ethyl, and isopropyl alcohol vapors at pressures below one atmosphere. Their results confirm the observation based on vapor heat-capacity studies that the fourth virial coefficient is more important than the third.

Conclusion

One feature that is particularly evident in a survey of present-day chemical thermodynamics is the fundamental importance of careful experimentation and accurate measurement. It seems appropriate, therefore, that this chapter, which was introduced by mention of Lavoisier, should end with a direct quotation from the "father of chemistry" which seems to apply as well to twentieth century chemical thermodynamics now as it did to eighteenth century general chemistry when it was written.

> This is a vast field for employing the zeal and abilities of young chemists, whom I advise to endeavor rather to do well than to do much. . . . Every edifice which is intended to resist the ravages of time should be built upon a sure foundation; and, in the present state of chemistry, to attempt discoveries by experiments, either not perfectly exact, or not sufficiently rigorous, will serve only to interrupt its progress, instead of contributing to its advancement.[2]

[2] Modernization of the translation of Robert Kerr.

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CRYOGENICS[1]

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This is the second article on cryogenics in the *Annual Review of Physical Chemistry*. The first, in the *Review* for 1953, set a pattern of limiting the treatment of cryogenics to a few related areas in order to cover these in more detail. Last year's review covered liquid helium, heat capacities, heat and electrical conduction (exclusive of superconductivity) and suggested that superconductivity and magnetic phenomena be covered in 1954. This suggestion has been followed. Next year, a review of the Third Law of Thermodynamics may be expected.

Superconductivity

Superconductivity is the name for the class of phenomena associated with an abrupt loss of electrical resistance at a fairly well-defined transition temperature, T_c. It is a low temperature phenomenon, the highest known superconducting transition temperature being 18°K. for Nb_3Sn (1).

Because of the availability of an extensive bibliography on superconductivity in *Physics Abstracts* (2), only a limited bibliography is included here. The intent of this review is to summarize research that portrays present understanding of the phenomenon. References to textbooks are included (3, to 6).

The superconductivity of Hg was discovered by Kamerlingh Onnes in 1908. Until 1933 it was thought that the superconducting state was described completely by: ρ (electrical resistivity) $=0$. Meissner & Ochsenfeld (1a) discovered that superconductors expel magnetic flux B and that ideal superconductors (pure and mechanically perfect) are completely diamagnetic; i.e., $B=\mu H=H(1+4\pi\chi)=0$, except for a thin layer at the surface of the superconductor. H. and F. London (5) showed that the Meissner effect (expulsion of B) is not explained simply by $\rho=0$. They developed a phenomenological theory in which Ohm's law for the normal resisting state is replaced for the superconducting state by curl $(\Lambda \mathbf{j}_s)=\mathbf{H}/c$, and $\partial(\Lambda \mathbf{j}_s)/t\partial=\mathbf{E}$, where $\mathbf{H}$ and $\mathbf{E}$ are the intensities of the magnetic and electric fields, $\mathbf{j}_s$ is the intensity of the superconducting current and Λ is a characteristic of the superconductor. The penetration z of H into a superconductor is: $H_{z=0}\exp(-z/c\sqrt{\Lambda/4\pi})$. An empirical relation for $c\sqrt{\Lambda/4\pi}\equiv\lambda$ is: $\lambda=\lambda_0[1-(T/T_c)^4]^{-\frac{1}{2}}$. For Sn, $\lambda_0\sim5\times10^{-6}$ cm.; for Hg, $\sim4\times10^{-6}$ cm., and for Pb, $\sim13\times10^{-6}$ cm. (7, 8). The dependence of λ on H is small: $(\lambda_{H=Hc}-\lambda_{H=0})/\lambda\sim0.01$ to 0.02, except within 0.1 degree of T_c, where it increases in an apparently exponential manner (9).

The superconducting state is destroyed and normal resistance reestab-

[1] The survey of literature pertaining to this review was completed in January, 1955.

lished not only by exceeding the transition temperature T_c, but also by exceeding critical values of the magnetic field at the surface of the superconductor, or of the current flowing in the superconductor. These critical values, H_c and I_c, are functions of temperature. $H_c = H_0[1-(T/T_c)^2]$ is an empirical formula with small deviations (10). The Silsbee hypothesis says that the magnetic field of I_c at the surface of the superconductor equals H_c. The H_c-curve in an H versus T graph is an equilibrium line in a two-phase (superconducting and normal resisting) diagram for the metal.

Only ideal specimens (pure single crystals) exhibit a complete Meissner effect ($B=0$ inside the superconductor) and fit the Silsbee hypothesis exactly. Alloys, especially two-phase alloys, show only a partial Meissner effect, and the critical magnetic fields for restoring normal resistance, for penetration of magnetic flux into the bulk of the metal, and for the critical current are all different. The superconducting properties of intermetallic compounds and single-phase alloys approach those of ideal superconductors as the specimens approach the ideal state of uniform composition and physical purity (11). Two-phase alloys and other nonideal superconductors, such as polycrystalline and strained metals and nonuniform single-phase alloys, are thought to form mixtures of superconducting and normal-resisting phases. Mendelssohn (3) suggested that structurally alloys resemble sponges with normal-resisting metal surrounded by superconducting meshes having higher critical fields than the metal enclosed. The magnetic flux in an alloy, when it enters the superconducting ($\rho=0$) state, is trapped in normal-resisting metal by the superconducting meshes. For ideal superconductors, critical values of the magnetic field at 0°K., i.e., H_0, are of the order of hundreds of oersteds (<1000). For alloys (*a*) the critical field for return of normal electrical resistance is of the order of thousands of oersteds [the highest value known being 22,000 oersteds for the Pb-Bi eutectic (12)], (*b*) the critical field for penetration of flux in the Meissner effect is of the order of hundreds of oersteds i.e., comparable with the critical fields for ideal superconductors, and (*c*) the magnetic fields of critical currents are only a little smaller than the critical fields for the Meissner effect (4).

The extent of superconductivity.—Of the chemical elements, 22 are known to become to superconducting. Transition temperatures T_c range from 0.35°K. for Hf (13) to 11° for Tc (14). See Eisenstein (15) for a critical review of T_c and H_c data for the elements. About 100 binary alloy systems are known to become superconducting. Transition temperatures range up to 18°K. for Nb_3Sn (1). The great majority of these alloys, but not all, have at least one superconducting component. Examples of superconducting alloys consisting only of nonsuperconducting elements are the following: Au_3Bi (16); CuS (17); Bi_2Pd (18); Bi with Li, Na, K, Ca, and Ni (19); Mo with Si and Ge (20) and with Ir (21); and Rh with W, Se, and Te (21).

It is thought that superconductivity is not a property of all metals, because (*a*) All known superconductors are normal conductors (R increases with T) at higher temperatures. Semiconducting grey Sn is a nonsupercon-

ductor (22), whereas white-Sn is a superconductor. Semiconductors PbS and PbTe are not superconductors (23); (*b*) All superconductors fall within a limited range of atomic volumes; (*c*) No ferromagnetic element is a superconductor; (*d*) The theories of Bardeen (24) and Fröhlich (25) for superconductivity include criteria limiting it to some of the metals.

The correlation of transition temperatures T_c with other properties.—Superconducting transition temperatures T_c are dependent upon crystalline structure, atomic weight, the number of valence electrons and, probably, the number of conduction electrons per atom.

Two examples showing that T_c depends on crystal structure are these: (*a*) The T_c of Bi_2Pd (monoclinic) is 1.70°K., and of Bi_2Pd (tetragonal) is 4.25°K. (18); (*b*) Normally, Bi is a nonsuperconductor, but, in a different allotropic form, at a pressure of from 2 to 4×10^4 atm., it becomes superconducting at 7°K. (26). Also, Bi-films condensed at 4°K. from vapor and kept cold are superconducting at 6°K.; they become nonsuperconductors when annealed above 30°K. (27, 28, 29).

The ratio T_{c1}/T_{c2} equals $\sqrt{M_2/M_1}$ for superconducting isotopes with atomic weights M_1 and M_2 (30a, 30b). De Launay (30c) attributes small departures to deviations of the energy density of the lattice-vibration spectrum from proportionality to a simple power of the frequency.

Matthias says (31) that the transition temperatures of annealed superconductors (pure metals and alloys) having the same crystal symmetry are proportional to $V^n \cdot f(r)$, where V is atomic volume, n has a value between 5 and 10, and r is the number (average for alloys) of valence electrons per atom. The function $f(r)$ is 0 for $r=1$ (column I of the Mendeleeff table), rises to a maximum for $r=5$ (column V), falls to a near zero minimum for $r=6$ (column VI), rises to a second maximum for $r=7$, and falls to a lower value at $r=8$. Compression lowers the transition temperatures of superconductors and tension raises them. Tl seems to be an exception (26, 32).

Hilsch & Buckel (27, 28) condensed microcrystalline films 5 to 50×10^{-6} cm. thick of Al, Zn, In, Tl, Pb, Hg, Ga, Bi, and alloys of Sn with Cu on crystalline quartz at 4°K. The Bi film was superconducting ($T_c=6$°K.). T_c for the Ga film was 8.4°K. (1.07°K. for bulk Ga) and the ratio T_c (film)/T_c (bulk) for the other films ranged from 0.94 for Hg to 2.26 for Al. The ratio T_c (film)/T_c (bulk) was a linear function of the Debye-Θ's for the bulk metals. On annealing, all the films underwent changes in their lattice spacings and in their normal electrical resistance after which the normal T_c's of these metals in bulk were observed. This investigation, also, demonstrates the importance of atomic volume and crystal structure.

Size effect.—In zero magnetic field, evaporated and annealed films as thin as 5×10^{-7} cm., and colloids of radius as small as 10^{-6} cm. have the same transition temperatures as bulk metal. In magnetic fields, however, there are size effects if the thickness is less than 10^{-4} cm., because the field penetrates the specimen to a depth of 10^{-6} to 10^{-5} cm. at 0°K. and to greater depths at higher temperatures, especially at the transition where the penetra-

tion becomes an order of magnitude greater. The critical magnetic fields of very small specimens are much higher than for bulk metal; for example, H_c (thin)/H_c (bulk) is about 10 for Sn and Hg films $\sim 5 \times 10^{-6}$ cm. thick (4). The penetration of magnetic fields in superconductors has been investigated through studies of the magnetic properties of colloids and thin films. Ginsburg & Landau (33, 34) developed a modification of London's phenomenological theory (5) in order to relate the surface energy of superconductors and the penetration of the field in a fundamental way, and to deal with the magnetic properties of thin films (35). The properties of sputtered and unannealed films are not the same as those of annealed films (27, 28 29, 35).

The high-frequency resistance.—There is no difference between the optical absorption and reflection of metals for infrared and higher frequency radiation in the normal and superconducting states. Thus, somewhere between D.C. and optical frequencies a radical change in the behavior of superconductors takes place. At frequencies of the order of 10^{11} c./s. the h.f. skin depth and the penetration depth λ of a superconductor are comparable as are also the magnitudes of the normal and superconducting components of the h.f. current in the skin (5). At frequencies $>10^{11}$ c./s. the h.f. skin is less than the penetration depth λ of a stationary magnetic field. The flow of normal current then becomes dominant and the superconducting component of the current disappears. Recent determinations (36, 37) of the h.f. absorption have been made from 10^8 to 3.5×10^{10} c./s. by measuring the Q-factors of h.f. resonating cavities containing superconducting metal. At 10^7 c./s. the absorption is too small for detection, but at frequencies $>10^8$ c./s. absorption is detectable and the h.f. resistance does not disappear at the normal transition temperature T_c. There is a gradual falling off of h.f. resistance of a superconductor below T_c. Though the h.f. absorption and resistance decrease with decreasing temperature they are finite and still measurable at the lowest temperatures reached. Increasing the frequency decreases the loss of h.f. resistance on passing T_c until there is no loss of resistance at all for optical frequencies. It is interesting that the frequency and temperature limits to superconduction are related by: $h\nu \sim kT_c$, so that for a T_c of 5°K., $\nu \sim 10^{11}$ c./s.

The intermediate state.—Only ideal superconductors (chemically pure, long needle-like, single crystals oriented parallel to the external magnetic field) make the superconducting transition abruptly. Specimens with other shapes, or inhomogeneites in composition or structure, pass through an intermediate state between the superconducting and normal states. In the intermediate state the specimen is a mixture of superconducting and normal-resisting regions, laminar or thread-like, oriented parallel to the magnetic flux in the specimen. This structure is fine-grained; for a tin specimen in a field $H/H_c \sim 0.8$ the thickness of the superconducting domains is of the order of a few tenths-millimeter. As a new state, superconducting or normal, is approached the domains of the new phase thicken while the others shrink.

For a discussion of the determinations of the structure of the intermediate state prior to 1952 see (4). For more recent investigations see (38, 39). How the domains end on an exposed surface of a superconductor is of interest because sharply bent lines of flux at the surface of a superconductor are supposedly unstable (40, 41). Were it not for a positive interfacial surface energy making the Gibbs function of the mixture of domains more positive, a fine-grained mixture of superconducting and normal domains, permitting magnetic flux to pass through the specimen without distortion, would be thermodynamically more stable than a pure superconducting state with Meissner effect. Through investigations of the intermediate state, the interfacial surface energy α has been determined. There is a characteristic length parameter for surface energy, $\Delta \equiv 8\pi\alpha/H_c^2$, which is about 4×10^{-5} cm. Unless the dimensions of a specimen are large compared with Δ ($>100\Delta$), properties in the intermediate state are dependent on the size of the specimen.

Supercooling and superheating.—The superconducting⇋normal-resisting transition has a hysteresis which is larger for specimens that are chemically and physically purer (4, 42). Usually, supercooling and superheating of a superconductor are investigated at constant temperature by varying the magnetic field. Faber (43) observed degrees of supercooling, defined by $|1-(H/H_c)^2|$, up to 0.8, and superheating up to 0.03. The transition is initiated at flaws in a specimen, where the surface energy is negative. The initial negative surface energy promotes the initial growth of a nucleus and enables it to attain a size where the increase of the normally positive energy of its growing surface is outweighed by the decrease of G (Gibbs function) of the metal transformed, and normal growth can proceed. After a nucleus is able to grow normally, the speed of propagation of a transition is limited mainly by the eddy currents generated by the changing of the magnetic flux B in the newly-transformed regions. Faber's experiments show that the velocity of growth ($\sim$10 cm./sec.) is proportional to $[(H_c-H)/H_c]^3$.

Thermodynamics of superconductors.—The ideal superconducting⇋normal-resisting transition is perfectly reversible and thermodynamic principles and equations are applicable. A transition without a complete Meissner effect is not perfectly reversible since an infinite number of different states of magnetization B are possible for the same values of the state variables H and T. Using (*a*) $[G_n(H,T)-G_s(H,T)]=(H_c^2-H^2)/8\pi$, (*b*) the empirical relation for $H_c(T)$, and (*c*) the thermodynamic equations for diamagnetic media, the heat of the transition in a magnetic field and the difference between the heat capacities of superconducting and normal-resisting metal have been deduced for ideal transitions without the use of any molecular model for the superconducting state. Mendelssohn & Moore found that when a large flux B is frozen in a superconductor (very little Meissner effect), which can happen with 2-phase alloys, little or no change in heat capacity of the metal is observed at the transition to the normal-resisting state. This indicates that a superconductor with much frozen-in flux consists mainly of normal-resisting domains (44). Normally, the latent heat of the supercon-

ducting transition in a magnetic field is spread over the range of the intermediate state.

The 2-fluid model.—In 1934, Gorter & Casimir (45) proposed a model for the superconducting state that is very similar to the 2-fluid model for He II. "Normal" and "superconducting" electrons of a superconductor correspond to the normal and super-fluid components of liquid He II. The 2-fluid model provides a useful picture of the superconducting transition as a "condensation" process in which electrons enter a lower-energy, zero-entropy state. The energy gap ϵ between superconducting and normal electrons is assumed to be independent of T and H. From calorimetric heat-capacity data Corak *et al.* (46) deduced that the ratio of the numbers of normal and superconducting electrons is proportional to a Boltzmann factor, $\exp(-\epsilon/kT)$. The model correlates nicely the thermodynamic and magnetic properties of superconductors. When London's field equations are introduced, it yields the observed dependence on T of the depth of penetration λ of the magnetic field below the surface of an ideal superconductor. Specific heats of normal electrons calculated from magnetic data agree fairly well with calorimetrically-determined electronic specific heats. Bardeen (47) has used the 2-fluid model with an extension of the London field equations for a calculation of boundary effects in superconductors. Marcus & Maxwell have presented the 2-fluid model in its most general form (48).

Heat conduction.—Since (*a*) conduction electrons are the principal carriers of heat in metals, and (*b*) conduction electrons in superconductors are condensed in a zero-entropy state, it is to be expected that the thermal conductivities κ_s of metals in the superconducting state would be less than κ_n in the normal state ($H > H_c$). Far below T_c practically all conduction electrons are condensed in the superconducting state, and Debye lattice-waves (phonons) are the principal conveyors of heat (49, 50, 51). Below 0.5°K., where $\kappa_n/\kappa_s \sim C/T^2$ for Sn, In, and Pb, it has been found that C is 350 for pure Sn, 115 for pure In, and 100 for Pb. The principal carriers of heat in some alloys are the lattice waves (phonons) even in the normal state. If the principal source of thermal resistance in such alloys is scattering of the phonons by conduction electrons, the condensation of electrons in the superconducting state increases the thermal conductivity and $\kappa_s > \kappa_n$. Such alloys do exist (4). The thermal conductivity of the intermediate state is frequently lower than that of either the superconducting or normal-resisting state because of the scattering of phonons by the many boundaries separating the superconducting and normal domains of the intermediate state. An important paper by Hulm (52) analyzes the experimental data for superconductors in terms of the heat conduction theories of Wilson and of Makinson.

Mathematical theory.—The most successful theories are those of Bardeen (53) and Fröhlich (54), which, though different in their mathematical formulation, are so much alike in their physical basis that they are often referred to as the Bardeen-Fröhlich theory. The motions of superconducting electrons and Debye-lattice waves are coupled, so that waves of charge density

move in phase with the Debye waves in a superconductor. Landauer (55) observed small changes in the elastic moduli of Sn entering the superconducting transition, indicating a lessening of the speed of sound in the super conducting state—an expected consequence of this coupling. The interactions of electrons and lattice vibrations at ordinary temperatures generate the ohmic resistances of pure, single crystals. In order for this electron-lattice coupling to produce an ordered state of lower energy in a superconductor it is necessary that (*a*) the temperature be low, (*b*) the electron-lattice interaction be sufficiently great (i.e., for the normal resistance of the metal to be sufficiently large), and (*c*) the density of conduction electrons be high (high valency, small atomic volume). The theory (*a*) explains the isotope effect (a larger amplitude of lattice-wave in a lighter isotope increases the coupling and raises its T_c) and (*b*) includes the Meissner effect in a qualitative way. The theoretical criterion for superconductivity is not completely satisfactory; the semiempirical criterion of Groetzinger *et al.* (56) is better.

Magnetism

Introduction.—The field of magnetism at low temperatures may be subdivided under headings of diamagnetism, paramagnetism, antiferromagnetism, and magnetic cooling. The subject of paramagnetism will be discussed in a brief section on paramagnetic resonance and within the section on magnetic cooling. The latter will also treat antiferromagnetic phenomena below 1°K., but those occurring in the liquid helium region and above will be omitted (see 57), as also will the entire subject of paramagnetic relaxation (see 58).

Diamagnetism.—The diamagnetism of strongly-bound electrons does not fit into the field of cryogenic physics; the diamagnetism of conduction and quasi-bound electrons, especially the oscillatory variations in the susceptibility observed originally in bismuth by de Haas & van Alphen (59), does fit, however, especially from the historical point of view. Theories of the effect were originally formulated by Peierls (60), Blackman (61), and Landau (62) and have been discussed to some degree in standard textbooks (63). An excellent review of the subject up to 1952 has been given by Shoenberg (64).

It is well known that classically the susceptibility of an electron gas is identically zero (65). Quantum mechanically, however, the expression for the susceptibility per cm.^{3} is

$$\chi = -\frac{4\pi m\beta^2}{3h^2}\left(\frac{3N}{\pi V}\right)^{1/3}$$

where m is the electron mass, β is the Bohr magneton, N is the number of electrons in volume V, and h is Planck's constant. Moreover this expression is only valid for $\beta H \ll kT$, H being the magnetic field. When this condition is not satisfied, i.e., at high H and low T, the susceptibility is an oscillating function of H, which, in fact, becomes positive in certain ranges of H. This is the de Haas-van Alphen effect.

While the effect should be common to all metals it has only been observed so far in bismuth, zinc, gallium, tin, graphite, cadmium, indium, antimony, aluminum, mercury, thallium, beryllium, magnesium, arsenic, and, more recently, in lead. Of course, the free-electron theory for these multivalent metals is not valid, and a more accurate treatment must take into account the strong and anistotropic interactions of the electrons with the crystal lattice. A full theoretical treatment which includes both the effect of the crystal lattice and an external field has not yet been given.

The Landau formula in the modified form of Blackman, which is quite complicated and will not be quoted here [see, e.g. Shoenberg (64, 66)] does make allowance for the effect of the crystal field by the introduction of anisotropic effective masses for the electrons. While this procedure is open to criticism (67), it does provide a possible interpretation of experimental results by allowing a summation to be made over different groups of electrons with different degeneracy temperatures and different effective masses. Although it is often sufficient to consider only one such group of electrons, this is not always the case. Aluminum, for example, for which there are two periods which differ by a factor of about 18 in frequency, is an exception (64). In either case, comparison of theory and experiment is reasonably satisfactory and can yield important electronic parameters. There is often disagreement over fine details, however. Thus in the case of gallium (64) there is observable a small effect attributable to the spin paramagnetism of the electrons, and this requires further slight modification to the theory (68, 69).

At present, efforts are being made (66) to find the effect in monovalent metals, but so far without success. The difficulty is that the frequency of the oscillations is expected to be very rapid and the amplitude small. Quoting from Shoenberg (66), for copper in a field of 10^4 oersteds the period would be about 0.16 oersteds and the amplitude of I/H about 10^{-10}. At higher fields, e.g. 10^5 oersteds, the period increases to 16 oersteds and the amplitude to 2×10^{-5} at which level there is a good chance of finding it experimentally. Shoenberg produced a transient field of this magnitude by discharging a condenser through a coil, and he determined the susceptibility of the sample by measuring the emf. induced in a pick-up coil wound round the specimen. Although negative results were obtained with copper, silver, gold, and sodium crystals, the effect was demonstrated for the first time in lead.

Steady fields of up to 10^5 oersteds are now available in a few places (notably the Naval Research Laboratory, Washington, D. C.), and this should enable investigations to be made at still higher fields, for example by using them in conjunction with the technique used by Shoenberg.

For some time it has been known that anomalies exist in the field dependence of the low-temperature magneto-resistance of bismuth (70), and these have been linked (71) with the de Haas-van Alphen effect. Similar but somewhat less-pronounced results have been obtained for the magneto-resistance of zinc and cadmium (72). Recently the work in the magneto-resistance of

bismuth has been extended (73), and periodic effects also found for this element in the Hall coefficient (74, 75), the thermoelectric effect (76) and the thermal conductivity (77). For graphite the effects have been observed so far for the Hall coefficient and magneto-resistance (78).

Paramagnetic resonance.—The subject of paramagnetic resonance is a vast one and can only be dealt with adequately in a specialized review, such as has been given by Bleaney & Stevens (79). A brief outline here will not be out of place, however, since it is intimately linked with magnetic cooling, indeed with the whole field of magnetism.

The technique of microwave resonance has many applications today in the field of solid state physics, and it has been employed with great success in the study of energy levels in paramagnetic ions, notably by Bleaney and co-workers at Oxford. The degeneracy of the levels is lifted by means of an externally-applied magnetic field, and the splitting pattern is modified by the effects of the lattice electric field. Transitions between the various levels occur when microwave power is applied to the crystal in a resonant cavity and the external field satisfies the condition $h\nu = g\beta H$. Dipole interactions broaden the resonances, and it is often necessary, especially in studying hyperfine structure, to dilute the crystals with nonmagnetic ions in order to achieve a satisfactory resolution. It is generally assumed that such dilution leaves the crystalline field splitting unaffected, but this is not invariably true. Magnetic hyperfine structure (h.f.s.) in the solid state was first observed by Penrose (80) in a copper Tutton salt. In strong magnetic fields, each electronic transition is split into $2I+1$ approximately equally-spaced lines of equal intensity. The levels may be further modified by the electrostatic interaction between the electric quadrupole moment of the nucleus and the gradient of the electric field at the nucleus. This effect was first observed by Ingram (81) in 1949 in a diluted copper Tutton salt, but in ionic crystals it is generally too small to be detected. The resonance data is of paramount importance to work on nuclear alignment, which is discussed below.

Magnetic cooling, introduction.—The only practical method of producing a significant lowering of temperature below 1°K. is "magnetic cooling" (82, 83). This makes use of the fact that certain salts exhibit paramagnetism and obey the Curie Law even in the liquid helium region. The entropy associated with the random orientation of the ionic magnetic moments may be largely removed in magnetic fields of 10 to 30 kilo-oersteds at 1°K., and upon isentropic demagnetization, the temperature will fall to such a value that the weak restraining forces within the crystal (electric or magnetic) can produce the same degree of order as was achieved by the strong external field at 1°K.

The paramagnetic coolant plays three roles in this process: first, enabling one to reach a very low temperature; second, providing a usefully large heat capacity; and, third, giving an indication of the temperature through its susceptibility or other magnetic properties. The lowest temperatures are reached when the salt is used to cool only itself, of course, and the phenom-

ena which may then be observed are discussed below; but by suitably proportioning the components, cooling-by-mixture may be applied to bring nonmagnetic substances into the region below 1°K. Without going into a lengthy discussion here of the problems of thermal equilibrium thus entailed, one may observe that there would be no problem for zero heat influx, and the departure from equilibrium depends primarily on the quality of the thermal insulation, and also upon the nature of the experiment and the temperature at which it is being performed. A large number of diversified experiments have now been carried out below 1°K. (see 84).

Behavior of paramagnetic salts below 1°K.—The most suitable salts derive their magnetic properties from ions of the first transition (iron) group or the rare earths and contain large amounts of water of crystallization which has the effect of magnetic dilution, and the consequently weak interionic forces result in the persistence of Curie Law behavior down to low temperatures. Deviations appear below 1°K. and increase rapidly below a few tenths of a degree; eventually a maximum in the susceptibility is reached, followed by a slow decrease with further decrease of temperature. On the low temperature side of the maximum, hysteresis effects are observed (85) and some sort of spatial ordering sets in, most probably antiferromagnetic in nature.

There are three kinds of interaction which produce the departures from the Curie Law below 1°K., viz. the effect of the electric field of the crystal lattice, the magnetic interaction between ions, and exchange interaction between ions. The latter is most probably "indirect exchange" (86) since the dilution is such that "overlap" of the magnetic ions is negligible. The situation is most readily described in terms of a concrete example, for instance the chromic ion, Cr^{+++}, in the alums. The free ion is in a $3d^3\,{}^4F_{3/2}$ state, but the electric field of the crystal interacts strongly with the orbital moment and produces fine-structure separations of the order of 10^4 cm.$^{-1}$, with a singlet level lying lowest. The level is fourfold degenerate by virtue of the spin. At low temperatures the ion is consequently effectively in a ${}^4S$ state (quenching of the orbital angular momentum) since the higher orbital levels are not occupied. If the lattice electric field were truly cubic this remaining fourfold degeneracy would not be lifted, but a small component of lower symmetry (trigonal) acts via spin-orbit coupling to produce a separation into two doublets lying about 0.2 cm.$^{-1}$ apart. It is this small splitting which brings about the departure from the Curie Law just below 1°K. At temperatures in the region 0.001° to 0.01°K. the entropy falls to R ln 2 as the upper spin doublet becomes depopulated. This remaining entropy is removed by magnetic (or exchange) interaction, which gives rise to the cooperative phenomena, e.g., characteristic specific heat anomaly, susceptibility maximum, and hysteresis. (Each drop in entropy produces a "specific heat anomaly" and by suitable choice of salt one may arrange, within limits, to have a large heat capacity at any desired temperature.)

A theoretical treatment of the problem was given by Hebb & Purcell (87), who determined the splitting-pattern in several specific cases. The

crystal field was handled by the method of crystalline potentials with reasonable assumptions as to symmetry, and Van Vleck's theory of magnetic dipole interaction (88) was included. They derived relationships between entropy and temperature, and susceptibility and temperature, and these were found to explain, in fair approximation, the experimental results available at the time down to about 0.1°K. Below this point the divergence became very large.

The technique of paramagnetic resonance developed in recent years now permits direct investigation of the energy-level pattern, and the old assumptions regarding crystal field symmetry have been found to be oversimplified in general. It is often found, further, that nuclear hyperfine structure plays an important part, e.g., in the Mn^{++} ion (89). The case of Cr^{+++} in potassium chromic alum remains a mystery since the resonance work shows two splittings, (90) which fact has yet to be explained. If one postulates two distinct sets of ions then the line-intensities are inconsistent with the shape of the specific heat curve. For the chromic ion in the methylammonium alum the splitting is found to be 0.180 $cm.^{-1}$ from resonance measurements,[2] whereas all workers employing the magnetic cooling procedure agree on the figure 0.192 $cm.^{-1}$ (91, 92, 93). It has been suggested that this might be a case where some indirect exchange is contributing to the specific heat. Somewhat paradoxically, this salt shows good agreement with the Hebb-Purcell theory over a wider range than does any other thus far investigated (93), and this theory takes no account of exchange interactions.

Below the temperature of the susceptibility maximum the magneto caloric effect [i.e.$(\partial T/\partial H)_S$] becomes negative. It follows that $(\partial S/\partial H)_T$ is positive, which fits the concept of antiferromagnetism since the first action of a small, increasing, external field will be to disrupt the antiparallel ordering and increase the entropy (94). The diagram of state (magnetic moment versus applied field at constant entropy, and equivalent plots) has been investigated for several salts (94, 95, 96) and found to agree qualitatively at least with theories of antiparallel ordering based either on both dipole interaction (97) or exchange interaction (98). Very good agreement could hardly be expected since the theories take no account of anisotropy effects, the presence of more than one ion in unit cell, and other complications.

Measurement of very low temperatures.—The problem of temperature measurement below 1°K. remains a challenging one. Temperature differences may be measured by a purely magnetic method (99). Most commonly, however, use is made of the Kelvin relation $T = dQ/dS$ and the experiments involve the determination of the ratio of the two quantities dQ/dx and dS/dx where x is a "thermometric parameter" such as the susceptibility. The problem centers on the difficulty of measuring dQ/dx: it is difficult to supply heat uniformly to the specimen and to correct for the effects of background heating, which is a surface effect. As a result, an arbitrarily nonuniform temperature distribution is achieved and x is no longer a unique func-

[2] J. M. Baker, Oxford (Unpublished data).

tion of the entropy. Various methods of heating have been employed by different workers such as γ-ray irradiation and a.c. losses, but agreement is usually bad. (For example, the Curie point of chromic potassium alum has been reported as 0.011°K. and 0.004°K. by Oxford (100) and Leiden (101) workers, respectively.) Presently existing discrepancies will probably be resolved when apparatuses are developed which can reproducibly achieve heat leaks of the order of 5 ergs/min. or less in specimens having a typical surface area of about 20 cm.^{2} To date, the most encouraging results have been obtained with methylammonium chromic alum, but here, too, it would be over optimistic to claim accuracy and reproducibility below about 0.08°K. The S-T correlations obtained by different workers agree quite well down to the lowest temperatures ($\sim$0.01°K.) but the χ-T relation, which is what the general user demands, varies quite markedly in the region of the susceptibility maximum. [The most easily-measured relation is that between χ and S and this is found to vary considerably in comparing the results of different workers. If single crystals are used, one observes that the susceptibilities become smaller over a period of time and this may be temporarily accentuated for any one series of experiments by carrying out the preparatory precooling to liquid nitrogen temperature rapidly (93). Even so, the smallest susceptibilities recorded are those obtained with a specimen made of compressed powder (92).]

The salt cerous magnesium nitrate is a special case in that it is found (102) to obey the Curie Law down to the egregiously low temperature of 0.006°K. Since this salt is strongly anisotropic, however, it can only be used in the form of a single crystal; it is, furthermore, of minor value as a cooling agent on account of its very small specific heat. [Strongly anisotropic paramagnetics have a particular value, however, in that, once such a substance has been cooled by adiabatic demagnetization, a magnetic field may be applied in the direction of small susceptibility without changing the temperature very markedly. Such a salt could, in fact, be cooled by simply magnetizing at 1°K. along the strong magnetic axis and then rotating the salt. It has been suggested (103) that the critical field of superconductors might be investigated in this way at low temperatures.]

Nuclear orientation.—In recent years methods have been developed for producing oriented nuclei. Two of the four methods (see *a*, *b*, *c*, *d*) which were proposed have been carried out successfully and have been put to use in the study of certain types of problem in nuclear physics. It is necessary in all four methods to work at temperatures in the range below 1°K. A distinction is drawn between two types of orientation; one is a polarization where there is a net nuclear magnetic moment, and the other is an alignment where, although orientations close to a given axis or plane are preferred, there is no distinction between parallel and antiparallel directions for the nuclear spins. The experiments which gave the first clear-cut demonstration of nuclear alignment were reported by Daniels, Grace & Robinson (104); similar experiments were reported shortly afterwards by Gorter *et al.* (105). The first

experiments in which a significant nuclear polarization was obtained were reported by Ambler *et al.* (106). The nuclei used in all these experiments were Co^{60}. Detailed discussions of the methods of low temperature nuclear orientation have been given by Simon, Rose & Jauch (107) and by Bleaney (108).

(*a*) The most direct way of orienting nuclei is to polarize them by applying a very large magnetic field at a sufficiently low temperature, and this is essentially the same problem as that of adiabatic nuclear demagnetization [Kurti & Simon (109), Gorter (110)]. The method is the most general in that it can be applied, in principle, to any type of nucleus with a nonzero magnetic moment. The degree of nuclear polarization which is set up is directly related to the entropy removed from the nuclear spin system. This has been discussed in some detail by Simon (111) who pointed out that to remove a significant amount of entropy, values of $H/T = 10^7$ oersteds deg.$^{-1}$ at least are needed. Since the biggest magnetic field which one supposes would be available for the purpose in the near future is about 10^5 oersteds, a starting temperature of 0.01°K. would be needed. A two-stage process would have to be carried out, therefore, in which the nuclear system would have to be cooled by contact with a paramagnetic salt, which had itself been cooled by adiabatic demagnetization.

Although it is now twenty years since this suggestion was made, a successfull experiment has not yet been carried out. The reason for this is that considerable difficulties, associated with the high contact resistances which prevail at low temperatures, are encountered in designing a thermal link which would be capable of transmitting the heat of magnetization from the nuclear stage to the electronic stage.

(*b*) A proposal was made, independently by Gorter (112) and Rose (113), that use could be made of the large magnetic field (10^5 to 10^6 oersteds) acting on nuclei of paramagnetic ions. This field arises from the orbital motion and spin of electrons in the unfilled magnetic subshell and can give rise to appreciable h.f.s. ($\sim$0.01 cm.$^{-1}$) through coupling with the nuclear magnetic moment. At a sufficiently low temperature ($\sim$0.01°K.), therefore, only the lowest hyperfine level will be populated, and this corresponds to an orientation of the nuclear magnetic moment with respect to the electron moment. Thus, polarization of the electron moments, which can be achieved at these very low temperatures by the application of a field of only a few hundred oersteds, results also in a polarization of the nuclear moments.

In principle the procedure is very simple. A suitable salt is magnetized at 1°K. in a field strong enough to saturate the electron paramagnetism, then demagnetized (the temperature falling in the process) to a few hundred oersteds. The method was tried by Gorter *et al.* (114) with ferric ammonium alum, but only a small and nonreproducible indication was obtained for the existence of a nuclear polarization. Later, however, it was effectively demonstrated by Bernstein *et al.* (115), who produced a nuclear polarization of about 17 per cent of the saturation value, using Mn^{55} in manganous ammonium sulfate.

It has been pointed out, however, that this method cannot be employed to produce very high degrees of nuclear polarization since the hyperfine splitting limits the lowest temperature which can be attained (108). We can see that magnetization at 1°K. will remove most of the entropy from the electron spin system but practically none from the nuclear spin system, whereas for high degrees of nuclear polarization we must remove as much entropy as possible from both systems. It was suggested by Gorter (116) that the salt under investigation could be cooled by contact with another salt having no h.f.s. Although in this case one encounters the difficulty of contact cooling below 1°K., the method has been used by Roberts *et al.* (117) to produce about a 12 per cent polarization of Sm^{149} nuclei. A more direct method of overcoming this difficulty is to incorporate in the same salt a second group of ions to produce cooling (118); these should, of course, have a very small h.f.s. or none at all.

Bleaney (108) pointed out that consideration of the electrostatic fields within a crystal is very important in choosing a salt for nuclear orientation purposes, since they can give rise to very strong forces which tend to align the electron spins. In many cases, therefore, the small externally-applied magnetic field would not be the dominant force acting on the electron spins.

(*c*) Bleaney (108) showed, however, that use could be made of this effect to achieve nuclear alignment in zero external field. It was this method which was used in the original experiments (104) on Co^{60}. The method relies on the fact that in certain paramagnetic salts, in particular the cobalt Tutton salts, the magnetic interaction between the unpaired electrons of the magnetic ion and the nucleus is anisotropic. The hyperfine splitting then depends not only upon the relative orientations of the electronic and nuclear spins, but also upon their orientation with respect to some axis of symmetry of the crystalline electric field. Alignment occurs at low temperatures when $kT \sim$h.f.s., and in zero external magnetic field. We have alignment rather than polarization because the energy of an ion is unaltered by reversing the directions of both nuclear and electron spins.

(*d*) Pound (119) suggested that the interaction between the nuclear electric quadrupole moment and an electric field gradient, which often produces considerable hyperfine splitting, might be used to produce nuclear alignment. Alignment is produced with respect to the gradient of the electric field, so that the crystal chosen should give rise to electric field gradients which are, for similar nuclei, similarly oriented within the crystal. In order that the field gradient should be big enough, the electron distribution around the nucleus should be very asymmetrical, such as is obtained in covalent bonds. The problem at present is to find a compound which fulfills the above conditions and, in addition, one in which the nuclear spin system can be cooled to a low enough temperature.

The experiments which have been carried out have used methods (*b*) or (*c*) and are of two types. One, for which only polarized nuclei can be used, comprises a study of the dependence of the capture cross section of slow neutrons on the relative orientation of neutron and nuclear spins; the other,

for which either polarized or aligned nuclei may be used, comprises a study of the anisotropy of γ-ray emission from radioactive nuclei.

Experiments of the first type have been carried out at the Oak Ridge National Laboratory using polarized Mn^{55} and Sm^{149} nuclei. In the Mn^{55} experiment, the change in capture cross section was determined when the direction of polarization of a slow neutron beam was changed from parallel to antiparallel with respect to the axis of polarization of the Mn^{55} spins. The change was measured by determining the difference between the numbers of radioactive Mn^{56} nuclei produced in the two cases. In the Sm^{149} experiment a somewhat different method was used; the results showed that for the 0.094 ev resonance level the capture cross section was greater when the neutron and nuclei spins were parallel than when they were antiparallel, and it was therefore concluded that the compound nucleus involved in the resonance has spin $(I+1/2)$, I being the spin of Sm^{149}.

Experiments of the second type, in which the angular distribution of γ-rays from aligned radioactive nuclei is determined, have been reported so far from Oxford, Leiden, and the National Bureau of Standards. This distribution is isotropic, of course, for a randomly-oriented system of nuclei but, in general, becomes anisotropic when there is some degree of nuclear orientation (120). The theory and the information obtained from such experiments is similar to that obtained from the now familiar angular correlation experiments (121), but the nuclear orientation method has a more general application; for example, it can be applied to nuclei where a single γ-ray is preceded by K-capture or an allowed β-transition, and it can be used to observe separately the polarized Zeeman components of a γ-ray. Techniques of handling the problem have been developed and general formulae given (122, 123, 124).

The angular distribution is found to contain only even powers of cos θ, where θ is the angle between the axis of quantization and the direction of emission, the highest power $\cos^{2n}\theta$ satisfying the condition that n is less than or equal to the spin of the initial nucleus, or the angular momentum carried away by the γ-ray (in units of $\hbar$), whichever is smaller. It is thus symmetrical with respect to a plane perpendicular to the axis of quantization, and it is therefore immaterial in these experiments whether we start with polarized or aligned nuclei.

The angular distribution will be a function of (*a*) the relative populations of the various magnetic substates, which will depend upon the h.f.s. and the temperature, and (*b*) the spins involved in the decay scheme. Thus, experiments may serve to determine hyperfine splittings and hence nuclear magnetic moments, and also to determine spins and spin changes.

The considerations which enter into such experiments are well-described in a paper by Bleaney *et al.* (125) in which Co^{60}-nuclei were aligned by method (*c*). Further experiments have been carried out by various workers on Co^{58} (126, 127), Co^{56} (128, 129), Mn^{54} (130, 131), Ce^{141} and Nd^{147} (132), and information about their decay schemes obtained.

It has also been established that, as expected, the γ-radiation from

aligned nuclei is polarized (127, 130). Such experiments can distinguish the character of the radiation (electric or magnetic), whereas intensity measurements can not. Further possible experiments, in which the sign of the magnetic moment of the initial nucleus could be determined by observing the state of polarization of the γ-ray, have been discussed by Steenberg (133) and Tolhoek (134). Limitations of space prevent any discussion here of the papers dealing with the newer resonance techniques which have been proposed to produce oriented nuclei, and we refer the reader to the original papers (135 to 139).

The helium vapor-pressure scale of temperature.—For experiments in the temperature range of 1° to 5°K., temperatures are usually computed directly from the vapor pressure over the liquid helium bath or indirectly from this by means of, for instance, a calibrated resistance thermometer. Until recently the "1948 scale" has been accepted for this purpose (140). This scale is a combination of the "1937 scale" [measurements of Schmidt & Keesom (141)] above 1.6°K., and the "1939 scale" [computed by Bleaney & Simon (142)] below this point. It was published in the form of tables by the Royal Society Mond Laboratory and made available to the various interested laboratories throughout the world. At the time of preparation, however, there was evidence from the work of Kistemaker (143) that the scale might be considerably in error in the neighborhood of the lambda-point and, to a lesser extent, between 2.2° and 4.2°K. Between the normal boiling point and the critical point the scale was drawn optimistically through five experimental points above 4.9°K. obtained by Kamerlingh Onnes & Weber (144).

In 1953, Erickson & Roberts (145) attempted a precise calibration of a magnetic thermometer in order to estimate the Curie-Weiss constant for manganous ammonium sulfate and found large deviations from a straight line when plotting χT against χ. They finally concluded that the explanation lay in the deficiencies of the 1948 scale, and as a result two deviation humps were found in a plot of $(T_{48}-T_{mag})$ against T. The 1948 scale appeared to be about 0.012° too high at the lambda point and about 0.005° at 3.5°K. These deviations have been confirmed qualitatively by various workers in the course of magnetic thermometer calibrations and in the accurate determination of specific heats, vapor pressure of He^3, etc. Worley, Zemansky & Boorse (146) obtained evidence of large errors in the 1948 scale above 4.2°K. using a carbon resistance thermometer, and Berman & Swenson (147)undertook a gas-thermometric determination of the p-T relation between 4.2° and 5.1°K. which confirmed the findings of Worley *et al.* as to the direction of the deviations but indicated the magnitude to be smaller, with a maximum of 0.02° at 4.9°K.

An early revision of the 1948 scale is highly desirable since it is no longer in universal use. It seems probable, however, that more work will have to be done before a general agreement can be reached.

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HETEROGENEOUS EQUILIBRIA AND PHASE DIAGRAMS[1]

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Each year the problem of reviewing in a few pages the large field of heterogeneous equilibria and phase diagrams becomes more difficult. The number of good papers in this field has increased each year as the practical value of the results has become apparent in such widely diverse fields as improvement of metals by alloying or heat treatment, substitution for critically scarce metals, ferrous and nonferrous slag metallurgy, surface finishing of metals, control of corrosion and oxidation of metals, glass making, development of high-temperature refractories, cement technology, geologic thermometry, the origin of rocks, minerals and ores, the separation and purification of solid and liquid organic compounds, the preparation and purification of chemicals, the utilization of natural products, the development of useful byproducts, and a host of other industrial developments. During this past year the literature has been particularly extensive because of the large number of good papers, published in Russian journals during the past few years, which have just become accessible this year by inclusion in the 1954 volume of *Chemical Abstracts*. More than 500 papers in the phase-equilibrium field were noted. In this review we have tried to mention, at least by subject matter, those which contain important pertinent data.

One of the best methods for presenting the results on heterogeneous systems is that proposed by Bogue & Newkirk (1) in their review of this subject two years ago in the *Annual Review of Physical Chemistry*. This method, based on chemical composition, divides the subject into five broad categories: (*a*) aqueous salt systems, (*b*) organic systems, (*c*) anhydrous salt systems, (*d*) metallic systems, and (*e*) oxides and refractory systems. Because of their long-range importance, we first of all call attention to the recent advances in graphical methods, theoretical studies, new experimental techniques and apparatus, and cite reviews of certain aspects of phase equilibria.

Graphical Methods and Theoretical Studies

Dolique & Lacombe (2) used the system SeO_2—ZnO—H_2O as an example of the advantages in the use of a right triangle instead of an equilateral triangle for the graphic presentation of ternary systems. A method of vectorial projection for phase diagrams was explained and illustrated by Krunchak (3). The quaternary systems, water—benzene—ethyl isovalerate—ethyl alcohol, and three other similar organic systems were studied by Chang & Moulton (4), who used a new graphical method with plait curves for pres-

[1] The survey of the literature pertaining to this review was concluded December 31, 1954.

entation of the data. Perel'man & Zvorykin (5) discussed the use of a prismatic heptatetroid and Perel'man (6) used a prismatic heptahedron to present data on the chlorides and sulfates of Na, K, and NH_4. Palkin (7) analyzed the phase diagrams of ten representative quaternary reciprocal systems presented in the form of a right-angle, three-sided prism, which can be considered the projection of a four-dimensional figure. When unfolded the prism appears as a flat hexagon. Such a system is formed by six salts derived from five ions. Dombrovskaya (8) used this same method to represent the system of the fluorides, bromides, and iodides of Na and K. Akhumov & Spiro (9) analyzed the use of logarithmic curves of solubility in quasi-binary phase diagrams, using $NaCl—MgCl_2—H_2O$, $NaCl—KCl—H_2O$, and $Na_2SO_4—NaCl—H_2O$ as examples.

Mikheeva (10) applied the law of mass action to an analysis of the structure of constitution diagrams of metals in a theoretical study of ternary systems with a single compound A_mB_n in equilibrium with the solid solution of the unreactive metal C and with an excess of either A or B. Kornilov (11) discussed the fundamental relations between metallic solutions and compounds and its effects on the prediction of phase diagrams. Voskresenskaya (12), on the basis of thermal quantities, found three classes of binary fused salt systems with a simple eutectic. Bulakh (13) made a theoretical study of systems with an incongruently melting compound.

Francis (14) examined the manner of coalescence of two separate binodal curves in ternary systems with a nonaromatic hydrocarbon, an aliphatic and an aromatic solvent with similar critical solution temperatures. Men'shchikov (15) discussed the use of conoidal diagrams in the study of ternary organic systems such as phenol—naphthalene—water. Świetoslawski (16) discussed the classification of ternary azeotropes in organic systems.

Reviews

The literature on solid solutions, beginning with Mitscherlich in 1819, was critically reviewed by Luzhnaya (17). A review of the constitutional diagrams of metal systems in which the sigma phase appears was given by Lena (18). Wendrow & Kobe (19) gave an excellent review of the hydrous alkali orthophosphate systems of Na, K, NH_4 and Li. Shears & Archibald (20) reviewed all phase studies on the industrially important $Al_2O_3—SiO_2$ diagram. The general principles and new research on the structural and thermodynamic relations between silicate systems and their possible models, particularly fluorine beryllates, were reviewed by Hahn (21). A comprehensive review and compilation of the solubility and vapor-phase data on the system $HCl—H_2O$ was made by Schmidt (22).

Apparatus and Methods

A book by Tsurinov (23) gives a historical review of temperature measurement and the Kurnakov pyrometer, with descriptions of equipment, installations and methods of differential thermal analysis. Wilburn (24) de-

scribed a completely automatic apparatus for differential thermal analysis. Kofler (25) used a microscope with a heating and cooling device in the stage to study organic binary systems. A centrifugal method for the separation of crystals and liquid in molten binary metal systems was described by Schellinger & Spendlove (26). Two methods were described by Hume-Rothery & Poole (27) for the determination of liquidus temperatures of alloys of Ti or other metals too reactive for use of conventional thermal analysis. Schofield & Bacon (28) used a method that reduced contamination by refractories for the determination of the melting point of Ti. Equipment for measuring electrical conductivity in systems of refractory borides up to at least 2000°C. was described by Glaser & Moskowitz (29).

Ravich & Borovaya (30) described a special autoclave for studying hydrous salt systems up to 650°C. and 350 atm. pressure. Vilím *et al.* (31) described a new flow equilibrium still for the determination of liquid-vapor equilibria for medium- and low-pressure ranges in organic systems. A simple vapor-liquid apparatus for organic systems by which exact data can be rapidly obtained was described by Costa Novella & Moragues Tarrassó (32). A self-adjusting, bridge-type controller for precise temperature control of furnaces at high temperatures was described from the U. S. National Bureau of Standards by Levin & Ugrinic (33).

Aqueous Salt Systems

Druzhinin & Shepelev (34) studied stable and metastable crystallization in $CaCl_2$—H_2O between 0° and 50°C. Solubility, viscosity, and specific gravity data on KI—KBr—H_2O at 0° ,15°, 35° and 50°, and on KBr—NaBr—H_2O at 0° and 25° were obtained by Mukimov, Kapkaeva & Bergman (35), and the first two authors suggested a method for the determination of viscosity and specific gravity of very viscous solutions studied in KBr—NaBr—H_2O at 0° and 25°C. Many ternary and quaternary systems of halides were studied as follows: KBr—KCl—H_2O, RbBr—RbCl—H_2O and RbBr—KBr—H_2O at 25° (36); sulfates and chlorides of K and NH_4 at 30° (37); $CaBr_2$—LiBr—H_2O at 25° and $BaBr_2$—LiBr—H_2O at 25° and 35° (38); $BaCl_2$—LiCl—H_2O, $SrCl_2$—LiCl—H_2O, $CaCl_2$—LiCl—H_2O at 25° (39); LiCl—$BeCl_2$—H_2O at 0° (40); LiCl—RbCl—H_2O and LiCl—CsCl—H_2O at 25° and 40° (41); $MgBr_2$—LiBr—H_2O (and the single salts with water) from 20° to ternary eutectic (42); $BaBr_2$—$HgBr_2$—H_2O at 4.5°, 10.4°, and 25° (43); $SrCl_2$—$CaCl_2$—H_2O between 18° and 114°, $SrCl_2$—$MgCl_2$—H_2O between 18° and 100° and $CaCl_2$—$SrCl_2$—KCl—H_2O between 18° and 114° (44). Linke (45) determined the nature of the hydrated phases and eutectics in the systems of Sr chlorate, bromate and iodate with water. $NaClO_4$—NH_4ClO_4—H_2O at 25° was studied by Karnaukhov & Druzhinin (46). High-temperature phase equilibria in NaCl—Na_2SO_4—H_2O were determined by Ravich, Borovaya & Ketkovich (47).

Several ternary and more complex systems of nitrates or nitrites were studied as follows: $Th(NO_3)_4$—HNO_3—H_2O at 25° (48); $Cr(NO_3)_3$—HNO_3—

H_2O at 5°, 15°, 25°, and 35° (49); polythermal data in H_2O—HNO_3—H_3PO_4 with Ca and NH_4 (50); $AgNO_2$—$NaNO_2$—H_2O at 25° (51); $Ca(NO_3)_2$—$Mg(NO_3)_2$—B_2O_3—H_2O at −30°, −20°, −10°, 0°, 20°, and 60°C. (52).

In the system H_2O—SO_3 Vuillard (53), by differential thermal analysis and heating curves, found a eutectic between ice and $H_2SO_4 \cdot 6H_2O$ at −62° and 29.3 per cent SO_3. The relations between H_2SO_4 and H_2SeO_4 and their monohydrates and tetrahydrates were studied by Kapustinskiĭ & Zhdanova (54). The system $Al_2(SO_4)_3$—H_2O between 0° and 100° was studied by Smith & Walsh (55). The solubility of K_2CrO_4 in aqueous ethanol solutions was measured by Linke (56) and that of $CaCr_2O_7$ in H_2O between 0° and 100° by Tarasenkov & Konopkina (57). The system $NaMnO_4$—H_2O from 0 to 96 per cent by weight of salt was studied from the ice point to decomposition temperatures by White & Miller (58). The following ternary or more complex sulfate systems were studied as follows: $Cr_2(SO_4)_3$—H_2SO_4—H_2O at 25° (59); $(NH_4)_2SO_4$—$(NH_4)_2SO_3$—NH_4HSO_3—H_2O at 30°C. (60); Na_2SO_4—$Al_2(SO_4)_3$—H_2O at 0° (61); Li_2SO_4—$(NH_4)SO_4$—H_2O at 0° and 25° (62) and at 0.1°, 71.8°, and 95.2° (63); polythermal studies of solid solutions in $CuSO_4$—$FeSO_4$—H_2SO_4—H_2O (64); $CuSO_4$—$FeSO_4$—$ZnSO_4$—H_2O at 27°, 49°, and 59° (65); $CuSO_4$—$NiSO_4$—$FeSO_4$—H_2O at 15°, 30°, 50° and 70° (66) the solubility isotherm at 25° in the sulfates and hydroxides of Cd and NH_4 (67).

Morey (68) determined the solubility up to the melting point of $NaPO_3$ and the vapor pressures of saturated solutions at 400° and 500° and at the two quadruple points in $NaPO_3$—H_2O. The solubility of normal Ca molybdate between 0° and 100° was measured by Spitsyn & Savich (69) and that of KH_2AsO_4 at different temperatures, including the transition temperature of the anhydrous salt to the monohydrate, was measured by Paul *et al.* (70). Stable and metastable solubilities of $CaHPO_4 \cdot 2H_2O$ and stable solubility of $CaHPO_4$ were determined at 25° by D'Ans & Knütter (71). Studies in the range 0.35 to 66 per cent and 1 to 60 per cent P_2O_5, respectively, were made at 25° in Fe_2O_3—P_2O_5—H_2O and Al_2O_3—P_2O_5—H_2O by Jameson & Salmon (72). ZnO—As_2O_5—H_2O, MgO—As_2O_5—H_2O, and MnO—As_2O_5—H_2O at 30° were studied by Takahashi & Sasaki (73). Measurements were made at 25°, 50°, and 80°C. in MgO—CaO—P_2O_5—H_2O by Belopol'skiĭ, Shpunt & Shul'gina (74). The system $AlPO_4$—H_3PO_4—H_2O was studied at 25°, 50°, and 75° by Brosheer, Lenfesty & Anderson (75).

Ravich & Borovaya (76) obtained p-x and p-t curves up to 500° in the aqueous system with chlorides and sulfates of K and Na. To regulate utilization of waste Na_2SO_4 from artificial silk manufacture Sakai & Seiyama (77) obtained phase data on Na_2SO_4—HCl—NaCl—H_2SO_4—H_2O. Itkina (78) obtained new data on Na_2CO_3—NaOH—H_2O, Na_2CO_3—NaCl—NaOH—H_2O, Na_2SO_4—Na_2CO_3—NaOH—H_2O, Na_2SO_4—NaCl—NaOH—H_2O, and Na_2SO_4—Na_2CO_3—NaCl—NaOH—H_2O at 100°C., and Itkina & Kokhova (79) obtained data on the last of these systems at 25°C. Bergman & Shakhparonov (80) obtained phase data in the range from −11.7° to

+35° in $KCl—KNO_3—NH_4H_2PO_4—H_2O$. In three papers Flatt *et al.* (81) obtained data at 25° on limiting quaternary systems and on the quinary system of water with nitric and phosphoric acids and Ca and NH_4, and showed a method of interpolation for establishing the coordinates of solutions saturated by two solid phases in a four-dimensional diagram. Perova (82) studied saturated solutions from 25° to the freezing point in $HBO_3—K_2SO_4—MgSO_4—H_2O$.

The solubility of $CaCO_3$ in water at various CO_2 pressures was measured by Schmitt & Schmitt (83) and Shternina & Frolova (84). The system $CaCO_3—MgCO_3—H_2O$ at 25° and 1 atm. pressure of CO_2 with water and with dilute NaCl solutions was measured by Yanat'eva (85) and by Sveshnikova (86). $Al_2O_3—H_2O$ between 25° and 900° was studied by Imélik, Petitjean & Prettre (87) and $In_2O_3—H_2O$ in the range 25° to 800° and 500 to 20,000 lbs./sq. in. pressure by Roy & Shafer (88). $Na_2O—Al_2O_3—H_2O$ was studied at 35° by Vol'f & Kuznetsov (89), $CaO—Al_2O_3—H_2O$ from 50° to 250° by Peppler & Wells (90) and at 20° with $CaSO_4$ as an additional component by D'Ans & Eick (91). For removal of H_2S and CO_2 from industrial gases Litvinenko (92) studied $H_2S—K$ or $Na_2CO_3—K$ or $NaHCO_3—K$ or $NaHS—H_2O$ in the temperature range 20° to 60°.

Tananaev & Nekhamkina (93) measured the solubility of $2KF \cdot AlF_3 \cdot H_2O$ in HF and the system $AlF_3—KF—H_2O$ at 25°. Other ternary systems reported were as follows: $NaF—B_2O_3—H_2O$ at 25° (94); $Na_2SiO_4—H_2SO_4—H_2O$ at 0° and 25° (95); $MgO—SiO_2—H_2O$ at elevated temperatures and pressures (96) and from 75° to 350° (97). Morey & Hesselgesser (98) determined the solubility of quartz in steam at 400°, 500°, and 600° at pressures up to 2000 bars; silica glass at 400° and 500°; the minerals albite and microcline at 500°, and enstatite at 600°; $CaSO_4$, $BaSO_4$, $PbSO_4$, Na_2SO_4, Fe_2O_3, SnO_2 at 500°, 1000 bars; and a series of natural sulfides at 500°. Wyart & Sabatier (99) measured the solubility of several forms of SiO_2 (quartz, tridymite, cristobalite, and glass) in steam at 400° and 480 bars.

Organic Systems

Grimes & Rowley (100) studied the system $C_6H_6—Et_2O—MgBr_2$ at 25°; Večeřa & Pinkava (101) the system cyclohexane oxime—$(NH_4)_2SO_4—H_2O$ at 80° and 90°. Mayper, Clever & Verhoek (102) studied the solubilities of *cis-* and *trans*-dinitrotetrammine cobalt (III) sulfates in water-dioxane mixtures at 15° and 25° in the range 0 to 71.5 per cent dioxane; Wittenberger (103) those of 1,5- and 1,8-anthraquinonedisulfonic acids in H_2SO_4 at 20°; Davies & Griffiths (104) those of α,ω-alkanedicarboxylic acids in benzene, in water, and in HCl solutions at a series of temperatures between 30° and 65°. Monblanova & Rodionov (105) determined the solubility of some β-amino acids in water at 25°. Failkov & Shevchenko (106) determined the solubilities and electrical conductivities of ammines of Ni, Zn, and Cd iodides with iodine in nitrobenzene and acetonitrile. Hölemann & Hasselmann (107) measured the solubility of acetylene in acetone as a function of

temperature and pressure from 3° to 40° and up to 30 atm. Warner (108) determined the solubility of $UO_2(NO_3)_2$, $Th(NO_3)_4$, and $Cu(NO_3)_2$ at 20° in nitromethane and in various alcohols, ketones, and other oxygenated organic solvents. Huffman & Iddings (109) measured the solubility of Zr thenoyltrifluoroacetonate (TTA) at 20°, 30°, and 40° in anhydrous benzene and in benzene saturated with water. Howland & Epstein (110) obtained two liquid phases at 0° in anhydous mixtures of Li and ethylamine.

Melting and solidification diagrams were obtained for a large number of systems as follows: CO_2—CH_4 (111); CO_2—$CClF_3$ between −30° and −80° and between 1 and 7 atm. pressure (112); CH_2BrCl—CO_2, CBr_2F_2—CO_2, $CBrF_3$—CO_2 (113); trifluoroacetic acid—water (114); N_2O_4—$MeNO_2$ (115); binary systems of diphenylamine with quinoline and with aniline (116); α-trinitrotoluene—1,8-dinitronaphthalene (117); 2,4,6-trinitrotoluene—1-nitronaphthalene (118); tetranitromethane—C_6H_6 (119); acenaphthene—5-nitroacenaphthene (120); binary systems of triphenylmethane with each of the following—thiophene, pyridine, PH_3CH—2-picoline, PH_3CH—3-picoline, PH_3CH—2,4-lutidine, naphthalene, 2-methyl naphthalene, and indene (121); binary systems of *p*-dibromobenzene with each of the following—picric acid, 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene, and picryl chloride (122); binary systems of camphor with each of the following—benzoic acid, naphthalene, *o*-chloronitrobenzene and *p*-dibromobenzene (123); camphor with β-sulfonates (*d* and *dl*) of *o*-, *m*-, *p*-chloroaniline and camphor with β-sulfonyl *o*-, *m*-, *p*-chlorophenylamides (*d* and *dl*) (124); 1-nitronaphthalene—2-nitronaphthalene (125); binary systems of acetamide with each of the following—H_2O, AcOH, pinacol, valeric, lauric, cyanoacitic, monochloracetic, trichloracitic acids (126); two-component solid solutions and eutectic systems in the systems of iodene, isoquinoline, naphthalene, and benzene and the binary systems of two-ring molecules with coumarone (127); Me palmitate—Et palmitate and EtOH—Et palmitate—H_2O (128); palmitic acid—stearic acid (129); *n*-vinylpyrrolidone—water (130); CO_2—ethane—ethylene between 140° and 180° K. (131); urea—resorcinol—hydroquinone (132); indene—naphthalene—C_6H_6 and indene—isoquinoline—C_6H_6 (133); urea—monoammonium phosphate—water from −15.3° to +40.0° (134).

Kravchenko (135) studied a large number of binary systems of phenanthrene with many benzene homologues and with indene and homologues of naphthalene. He found that the simple eutectic diagram predominates, solid solutions occur rarely and only in the systems phenanthrene with trinitrohydrocarbons do compounds occur. Penkala in three papers (136) confirms the contention that the eutectic points for a series of binary systems involving a common constituent lie practically on a monotonic, continuous curve and binary mixtures of a substance A with a series of homologues B_1, $B_2 \cdots B_n$ show a gradual change from eutectics (no solid solution) through eutectics with limited solid solution to unlimited solid solutions.

Vapor-liquid equilibrium was studied in the following: HCl—ethane (137); ethane—ethylene (138); nitromethane—nitroethane at subatmos-

pheric pressure (139); MeOAc—MeOH, MeOAc—H_2O, and MeOAc—MeOH—H_2O (more than 10 weight per cent H_2O permits separation of MeOAc and MeOH) (140); acetone—methanol (141); acetone—chloroform and benzene—acetone (142); 1-butylene—butadiene with MeOH or MeOAc (143); benzene—methanol, *PVT* relations between 150° and 300° (144); ethylbenzene—styrene at 100 mm. Hg pressure (145); ethylbenzene or styrene with diacetone alcohol and water at 25° (146); dimethylformamide with benzene or methanol (147); biphenyl—4,4′-dinitrobiphenyl (148); methanol—butyl sebucate at 18° and 20° (149); naphthalene—1-octadecene at subatmospheric to atmospheric pressure (150); *m*- and *p*-xylenes in 39 different commercial solvents (151); furfural—methanol—water (152); heptane—toluene—liquid NH_3 and heptane—pyridine—liquid NH_3 (153); water—isopropanol and water—isopropanol—H_2SO_4 at 25° (154); water—methanol—aniline—benzene at room temperature (155); heptacosafluorotributylamine with methylcyclohexane or isooctane (156).

The distribution of formic acid between water and methyl isobutyl ketone was determined by Vogt & Geankoplis (157) and of 8-quinolinol between water and chloroform at 25° by Moeller & Pundsack (158). The separation of benzene and hexane by means of ethylenenediamine as solvent at 20° was studied by Cumming & Morton (159). Francis (160) determined the mutual solubilities of liquid CO_2 with each of 261 organic substances.

Westwater & Audrieth (161) showed that *tert*-butyl hypochlorite and water are virtually immiscible but each is completely miscible with *tert*-butyl alcohol and that there is a solutrope formation at both 20° and 0°. Zil'berman & Skorikova (162) found that hexamethyleneamine and water at room temperature are completely miscible but at higher temperatures two conjugate solutions are formed with a completely closed solubility curve with maximum and minimum consolute points. Cox (163) found that 2-, 3-, and 4-ethylpyridine and 2:3-, 3:4-, and 3:5-dimethylpyridine are partially miscible with water and all six give solubility curves of the closed-loop type. Purnell & Bowden (164) determined the binodal curves and tie lines for ternary systems of Ph_2O and water with a series of alcohols and acids. Zil'berman (165) found that adiponitrile with water gives a binodal curve with a flat maximum, and also studied the same system saturated with NH_3. Atack & Rice (166) studied critical phenomena in the system cyclohexane—aniline, and Kreglewski (167) studied similar phenomena in the binary systems of pyridine with isobutyl or isopropyl or isoamyl alcohol. Sweitoslawski & Kreglewski (168) studied critical phenomena in acetone-chloroform.

Anhydrous Salt Systems

Many systems of halides were reported as follows: AlI_3—HCl—$AlCl_3$—HI at 25° (169); NH_3—BF_3 and $NHMe_2$—BF_3 at low temperatures (170); Br_2—BrF_3 at low temperatures shows an immiscibility gap which intersects BrF_3 solubility curve (171); Li, Na, K, Ag, Cs, Ni, Cu, Ba, Al, La, Zr, Th, Nb fluorides with BrF_3 at 25° and 70° (172); $AlBr_3$, $AsBr_3$, $SnBr_4$, and SnI_4

with BBr_3 (173); Cl_2—NOCl between −57.5° and −5° (174); Br_2—$CHCl_2$-CHF_2 and Br_2—$CHCl_2CF_2Cl$ (175); BF_3 in benzene and toluene (176); PCl_5—$AlCl_3$ and PCl_5—$FeCl_3$ (177); NOCl—$AlCl_3$ (178); $TiCl_4$ and $TiBr_4$ as solvents for a large number of metal halides (all simple eutectic systems) (179); $SnCl_4$ with $CH_2ClCOOH$ or CCl_3COOH or $CHCl_2COOH$ and $SbCl_5$—CH_3COOH (180); $AlCl_3$ with $SeCl_4$ or $TeCl_4$ (181); UF_6—HF (182); $TiCl_4$—$POCl_3$ (183); NaCl—KCl forms solid solutions which at lower temperatures unmix with an upper consolute temperature of 490° at 67 mole per cent NaCl (184); NH_4Cl—NH_4Br, NH_4I—KI and NH_4NO_3—$(NH_4)_2SO_4$ in range from −100° to +20°C. (185); LiF—BeF_2 (186); $MgCl_2$—$CaCl_2$ and $MgCl_2$—KCl (187); TlCl—$CdCl_2$, KI—HgI_2 and KNO_3—$K_2Cr_2O_7$ (188); Cd acetate—K acetate (189); KCl—$MgCl_2$—$CaCl_2$ (190); NaOH—NaI, NaOH—NaBr and NaOH—NaBr—NaI (191); $AlCl_3$—HCl—HBr—$AlBr_3$ at 24°, 40°, and 70° (192); fluorides and chlorides of Ba and K and of Ba and Rb (193); fluorides and chlorides of Ba and Li (194); the metals and metal chlorides of Bi and Ag (195); KCl—NaCl—$MgCl_2$—$CaCl_2$ (196); $CaCl_2$—$BaCl_2$—CaF_2—BaF (197); the fluorides, chlorides, bromides, and iodides of Na and K (five complex mutual system) (198).

The following nitrate or nitrite systems were reported: $NaNO_3$—KNO_3 (199); $NaNO_3$—$NaNO_2$ (200); KNO_2—KNO_3 and KNO_2—$NaNO_3$ (201); KNO_3—$AgNO_3$ (202); $LiNO_3$—$NaNO_3$—$Cd(NO_3)_2$, $LiNO_3$—KNO_3—$Cd(NO_3)_2$, $AgNO_3$—KNO_3—$Cd(NO_3)_2$ (203); $NaNO_3$—KNO_3—$Ba(NO_3)_2$ (204); $LiNO_3$—$TlNO_3$ and $LiNO_3$—KNO_3—$TlNO_3$ (205); nitrates and bromides of K and Na (206); nitrates and fluorides of K and Na (207); nitrates and chlorides of Li and Ag (208).

Many other anhydrous salt systems were studied as follows: sulfates and hydroxides of K and Na (209); sulfates and molybdates of Na and Pb (210) and of Na and Ag (211); chromates and hydroxides of Na and Li (212); K_2WO_4—$K_4P_2O_7$, Na_2WO_4—$Na_4P_2O_7$, K_2WO_4—Na_2WO_4 and part of K_2WO_4—Na_2WO_4—$K_4P_2O_7$ (213); $Ag_4P_2O_7$—$Na_4P_2O_7$ and $Ag_4P_2O_7$—$K_4P_2O_7$ (214); sulfates and chlorides of Li and Cd (irreversibly reacting system with immiscibility) (215); KF—KCl—K_2CrO_4 (216); chlorides and sulfates of Na and Zn (217), of Na and Li (218) and of Li and Co (219); chlorides and nitrates of Rb and Co (220); fluorides and chromates of K and Na (salt baths for metal treatment) (221); chlorides and carbonates of Na and Ba (222).

Russian investigators studied an extensive series of systems of titanates with carbonates and many other salts—$BaTiO_3$ with 26 different salts, up to 1200° (223); $PbTiO_3$ with 13 different salts, up to 1100° (224); $BaTiO_3$—Na_2CO_3—K_2CO_3 and $BaTiO_3$—$BaCO_3$—$BaCl_2$ (225). Karan & Skinner (226) determined the phase diagram for $BaTiO_3$—KF and the solid solubility of KF in $BaTiO_3$ between 1000° and 1300°.

Metal Systems

Only those papers can be noted here which have a major bearing on the constitution diagrams of metal systems.

Raynor *et al.* (227) studied alloys of Al and Zn with Fe, Co, and Ni, alloys of Al and Mg with Co and the systems Al—Mn—Fe and Al—Fe—Be. Phillips (228) determined the constitution of Al-rich alloys with from 0 to 40 per cent Cu, and 0 to 3.5 per cent Fe. Grube & Jauch (229) determined the diagram for Al—Pd by electrical conductivity, thermal and x-ray analysis, and microscopy. Hosoi (230) determined the liquidus surface of Al—Cu—Sn. Tournaire & Renouard (231) found it possible to follow quantitatively the development of the Mg_2Si phase in Al—Mg—Si alloys during aging by HCl treatment and to point out that differential-solution methods could be used to study constitution diagrams as well as the phenomena of precipitation hardening. Hofmann (232) studied alloys with up to 2 per cent Mn and 6 per cent Cu in Al—Cu—Mn and constructed isotherms at 400°, 525°, and 610°.

The constitution of Cu-rich Cu—Al—Ge alloys was determined by Raynor & Greenfield (233) and for Fe—FeSi—Cu_2Si—Cu by Vogel & Horstmann (234).

Many Hg alloy systems were studied as follows: Hg—In (solubility of In in Hg between 10° and 156.2°) (235), Hg—Na and Hg—NH_4 (236), Hg—La (237), Hg—Pt (238), Hg—U (whole composition range between −40° and +1000°) (239).

Abrikosov (240) studied the constitution of Cu—Be alloys in the ranges 3.75 to 16.6 and 53.4 to 83 atomic per cent Be. The use of specific heat data to determine phase diagrams was discussed for Pb—Cd, Bi—Cd and Sn—Bi by Nagasaki & Fujita (241). The preparation and constitution of Cu—B alloys was discussed by Lihl & Feischl (242). The constitution of Cu-rich Cu—Zn—Ga alloys was determined by Massalski & Raynor (243). With the thesis that solid solubility or absence thereof of various elements in Cr is determined by the chemical properites of the elements, Kornilov (244) discussed prediction of phase diagrams in Cr systems and indicated that similar reasoning could be applied to Mo and W systems. Bloom & Grant (245) investigated the Cr—Mo—Ni system and the limiting binaries. They completed the liquidus surface and a section at 1250° in the ternary, and suggest some revisions of the binaries. Shih & Peretti (246) determined the constitutional diagram of In—As—Sb from thermal, x-ray and metallographic data. Kornilov (247), from an analysis of the data on Fe systems, concluded that the temperature of formation of compounds on cooling of solid solutions increased with increasing separation of the other elements from Fe in the periodic table, either by column or row. Busby, Warga & Wells (248) and Nicholson (249) determined the Fe—B diagram in the low-boron range. Svirbley & Selis (250) determined the Ga—In phase diagram from resistance measurements. Hellner (251) studied the Ni—Ga system by x-ray methods. Thurmond & Struthers (252) measured the retrograde solubility of Sb in Ge, Cu in Ge and Cu in Si. Butuzov & Gonikberg (253) measured the rise in melting temperature with pressure up to 34,000 kg./sq. cm. for Sn and for Pb. Pasternak (254), by a relative electrical resistivity method, determined the solid solubilities of Ag, Cd, Mg and Zn in Pb and of Al, Bi and Cd in Zn.

Using the same method Kurzyniec & Wojtaszek (255) determined the solubility of Sn in Pb and Pb in Sn between room temperature and 100°, and the latter author determined that of Tl in Sn and of Sn in Tl up to 60°.

A new constitutional diagram for Ag—Li by Freeth & Raynor (256) differs considerably from previous diagrams, and diagrams for Mg—Li and Mg—Li—Ag were presented. Eremenko *et al.* (257) studied the systems Mn—Mo and Mn—Ni. Kornilov & Pylaeva (258) studied the equilibrium diagram of Ni—Ta between 0 and 59.04 per cent Ta. Wilhelm, Carlson & Dickinson (259) showed that in Nb—V there is a complete series of solid solutions with a minimum in the solidus at 1810° near 35 weight per cent Nb with no compounds or intermediate phases above 650°.

McPherson & Hansen (260) presented a bibliography and review of phase diagrams of 18 binary Ti alloy systems. McQuillan (261) made a redetermination and reinterpretation of the Ti-rich region in Ti—Cr and studied Ti-rich Ti—Au alloys. Eisenreich (262) measured the solubility of Ti in Mg, and Sutcliffe (263) that of Si in Ti. Worner (264) gave a phase diagram in the range 650° to 1100° for Ti-rich Ti—Ag alloys. Buzzard, Liss & Fickle (265) and Udy & Boulger (266) gave a diagram for the U-rich portion of the system Ti—U. Kieffer, Benesovsky & Schroth (267) gave a tentative diagram for Cr—Si. Elliott, Levinger & Rostoker (268) studied Ti—Cr—Mo alloys with 40 to 100 per cent Ti in the range 550° to 1300° and Ti—Mn—Mo alloys with 60 to 100 per cent Ti in the range 550° to 1150°. Ti-rich alloys in Ti—Al—O, Ti—Al—N, and Ti—Al—C (269) and Ti—Cr—O (270) were studied. A good review of recent work on Zr and its alloys was presented in a recent symposium (271). Kieffer, Benesovsky & Machenschalk (272) gave a literature review, a description of the vacuum sintering method for alloy preparation and a phase diagram for the range 1000° to 2400° for Zr—Si and some data on $ZrSi_2$—$TiSi_2$ and $ZrSi_2$—VSi_2.

Other interesting investigations reported were as follows: reconnaissance of systems of Ru, Os, Rh, Ir, Pd with W (273); solubility of U in liquid Na at 97.8° (274); diagram up to 1250° for U—Pb (275); survey of U—Ni system (276); phase diagram for Ag—U (277); phase diagram of Pd—Zn and Pd—Zn—Ag (278); reinvestigation of Au—Pt (279); revised diagram for Fe—Pt (280); reconnaissance of Mo alloys with up to 70 atomic per cent Mo with Ru, Rh, Pd, Os, Ir and Pt (281).

Some oxide, nitride, and carbide systems were reported as follows: solubility of O in α-Fe between 700° and 900° (282); solubility of Ag_2O in Cu_2O and PbO melts (283); constitution of Ti-rich alloys of Ti—Fe—O (284); x-ray investigation of the system Ta—O (285); diagram for Zr—ZrO_2 (286); phase diagrams for Cu—Cu_2O, Cu—Pb, Pb—PbO and Cu—Pb—O (287); solubility of O in Nb (288); phase diagrams up to 17.5 per cent N and 33 per cent B, respectively, in Ti—N and Ti—B systems (289); Ti—C—N and Ti—C—O systems between 500° and 1000° in the range 0 to 5 per cent N or O and 0 to 2 per cent C (290); new data on the Mo—C and Mo—Si—C

systems (291); phase diagram for the Ti—W—C system (292); Cr-poor side of WC—TiC—Cr_3C_2 (293).

Schlegel & Schüller (294) made a critical review of Cu—Fe—S, including the limiting binary systems and the numerous ternary compounds, and studied 150 synthetic melts. Kullerud (295) made a thermal and x-ray study of synthetic mixtures in FeS—ZnS and presented a phase diagram. Nowotny *et al.* (296), from x-ray data, determined the solid solubility at 1300° of $TiSi_2$ in $CrSi_2$ and studied the systems $CrSi_2$—$TaSi_2$ and Cr_3Si—Mo_3Si. Illarionov & Sokolova (297) studied the system P—S and gave an equilibrium diagram. Kushima & Asano (298) determined the phase diagram of the binary systems Ni_3S_2—Cu_2S, FeS—Cu_2S, and Ni_3S_2—FeS above 400°.

Oxides and Refractory Systems

Cirilli & Burdese (299) showed that limited solid solutions with 9.5 per cent CaO in FeO and 9.0 mole per cent FeO in CaO coexist with metallic Fe at the eutectic at 1120° at 30 mole per cent CaO in the system CaO—FeO. The compositions of compounds in the system CaO—Fe_2O_3 are still in controversy (300). Montoro (301) studied the distribution of the two metals between two valence states in mixed crystals in Fe_3O_4—Mn_3O_4 and Fe_2O_3—Mn_2O_3. Dietzel & Tober (302) made a reconnaissance of ZrO_2 systems with Li_2O, MgO, CaO, NiO, CoO, ZnO, and U_2O_5. Lambertson, Mueller & Gunzel (303) found a continuous series of solid solutions between UO_2 and ThO_2, and Lambertson & Mueller (304) found a eutectic at 2550° and 52.5 mole per cent ZrO_2 in UO_2—ZrO_2 with extensive solid solution and some polymorphism.

Budnikov & Cherepanov (305) made a fusion reconnaissance study of BeO—SiO_2. Bron & Podnogin (306) determined the melting point of Al_2TiO_5 at 1890° ± 10°. Other TiO_2 systems were studied as follows: BaO—TiO_2 (307); MgO—TiO_2, CaO—TiO_2, and ZrO_2—TiO_2 (308); ZrO_2—TiO_2 (309); CaO—TiO_2 (310); $CoTiO_4$—Zn_2TiO_4, Co_2TiO_4—Mg_2TiO_4, Co_2TiO_4—Co_2GeO_4, and other Co, Ni, Ge, Zn and Fe spinels (311); BeO—Al_2O_3—TiO_2 (312); CaO—Al_2O_3—TiO_2—SiO_2 (313).

In the system CaO—MgO—Al_2O_3, Repenko (314) determined liquidus data on those compositions which melt below 1600°. Brisi & Burdese (315) studied ternary solid solutions in CaO—MgO—FeO. Levin & Ugrinic (33) determined the phase diagram for BaO—B_2O_3—SiO_2 by the method of quenching, and Dietzel, Wickert & Köppen (316) that for Li_2O—BaO—SiO_2 by the same method. Krishna Murthy & Hummel (317) studied the Li_2SiO_3—β-eucryptite join in Li_2O—Al_2O_3—SiO_2. Dietzel, Wickert & Köppen (318) determined the phase relations in that portion of Li_2O—BaO—SiO_2 richer in SiO_2 than the metasilicates. Kukolev & Roĭzen (319) studied phase relations in the portion of CaO—Al_2O_3—SiO_2 with 2 to 6 per cent SiO_2 and 60 to 70 per cent Al_2O_3. Ricker & Osborn (320) obtained considerable additional phase information and located a field for $3CaO \cdot SiO_2$ in the ternary system

$CaO—MgO—SiO_2$. They found extensive solid solution at high temperatures between monticellite and forsterite but none between merwinite and monticellite. Segnit (321) studied the phase relations in the high-lime portion of $Na_2O—CaO—SiO_2$ and in a second paper reported on a study of $CaO—ZnO—SiO_2$ by the method of quenching.

The following interesting systems were also studied: liquidus surface of $FeO—MnO—SiO_2$ (322); fusibility diagram for $MgO—ZrO_2—SiO_2$ (323); the portion $FeO—FeO \cdot Cr_2O_3—2FeO \cdot SiO_2$ of $Cr_2O_3—FeO—SiO_2$ (324); isomorphism in the systems $In_2O_3—Y_2O_3—ZrO_2$ and $In_2O_3—Y_2O_3—CeO_2—ThO_2$ (325).

Schairer (326), from quenching data on five triangular joins, determined the phase relations in that portion of the system $K_2O—MgO—Al_2O_3—SiO_2$ lying in the volumes leucite—corundum—spinel—silica and leucite—forsterite—spinel—silica, and applied the results to geology and refractories. Prince (327) studied the plane with 10 per cent MgO in $CaO—MgO—Al_2O_3—SiO_2$. Herold & Smothers (328) studied solid-state equilibria in $MgO—Al_2O_3—ZrO_2—SiO_2$. Segnit (329) determined the solid solution limits of Al_2O_3, of Fe_2O_3, and of TiO_2 in synthetic diopside melts. Cole (330), in a historical review of glass compositions used for window glass, showed that such compositions have become stabilized to those in the system $Na_2O—CaO—MgO—Al_2O_3—SiO_2$. Karkhanavala & Hummel (331) studied the join cordierite—spodumene in $Li_2O—MgO—Al_2O_3—SiO_2$. Keith (332) determined the phase relations in $MgO—Cr_2O_3—SiO_2$ and Warshaw & Keith (333) those in the join $MgO \cdot Al_2O_3—MgO \cdot Cr_2O_3$ and in the silica-poor portion of $MgO—Al_2O_3—Cr_2O_3—SiO_2$. Berezhnoĭ (334) reviewed the system $CaO—MgO—Fe_2O_3—SiO_2$ and the three limiting ternary systems for compositions and properties of use in refractories.

Budnikov & Tresvyatskiĭ (335) found a eutectic at 1360° and 76.5 mole per cent CaF_2 in the system $CaO—CaF_2$. Roy, Roy & Osborn (336) studied the systems $LiF—BeF_2$ and $PbF_2—BeF_2$. The eutectics in the systems with cryolite and MgO, CaO, ZnO, CdO, and TiO_2 were determined by Hayakawa & Kido (337). A partial liquidus diagram for $FeS—FeO—SiO_2$ was given by Yazawa & Kameda (338). Portions of the systems $CaO—P_2O_5—Al_2O_3$ and $CaO—P_2O_5—Al_2O_3—SiO_2$ of interest in Portland cement were studied by Hartmann & Haegermann (339). The region of transparent glass formation in $Li_2O—MgO—B_2O_3$ was investigated by Mazelev (340), and Gode & Sīmane (341) made a reconnaissance of $Na_2O—SrO—B_2O_3$.

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SOLUTIONS OF ELECTROLYTES[1]

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Debye's seventieth birthday presented us with a collection of his papers (1), edited by I. Fankuchen, R. M. Fuoss, H. Mark, C.P. Smyth, and H. S. Sack. The reading of the papers on electrolytes will be a great pleasure for many, even though the English translation does not fully reproduce the elegance of Debye's German style.

Kraus (2) reviewed our ideas of electrolytes, our problems, and his numerous contributions to their solution. Bonhoeffer's survey (3) of work carried out in Goettingen contains numerous important comments but appeared too late for a discussion in the present review.

General Theory

Ionic interaction.—Two significant recent developments were extensively reviewed in the preceding volume of the *Annual Review of Physical Chemistry* (4). Progress has been achieved in the rigorous statistical mechanics of electrostatic interaction, and the idea of taking into account the proper volume of ions in the ionic atmosphere appears to be promising. In both directions further progress can be reported.

Kirkwood & Poirier (5) confirm the validity of the relation of Debye and Hückel as a first-order approximation of the solution of the Poisson-Boltzmann equation. The procedure of averaging Poisson's equation and the charging processes are correct. The first-order approximation behaves peculiarly at higher concentrations.

A higher approximation (up to $c^{1.5}$) in log γ has been derived by Haga (6) from Mayer's theory. Scatchard (7) discusses the magnitude of the various terms in Mayer's series and compares the results with the earlier extensions of the theory of Debye and Hückel proposed by Gronwall, LaMer & Sandved (8), Kirkwood (9), and Bjerrum (10). Scatchard's paper contains a good deal of important information compressed in few words.

Whenever relations for heat content and volume are derived from a more elaborate relation than the square-root limiting law, considerable difficulty is encountered. Benson's (11) application of the results of Mayer and Poirier to the heat content leads to a description of the available data by means of an additional empirical parameter, the temperature dependence of the ionic radius. No positive confirmation of the theory is achieved. Essentially the same situation was described by Gross & Halpern (12, 13) long ago. For the volume, Benson introduces the pressure dependence of the ionic radius as an empirical parameter. Moreover, he uses a questionable value for the pressure

[1] The survey of the literature pertaining to this review was concluded in December, 1954.

dependence of the dielectric constant of water, to be discussed in the section "Coefficients of the limiting laws."

A promising new development started a few years ago with a new distribution function proposed in somewhat formal terms by Bagchi (14). Dutta & Bagchi (15) showed that the deviation of this distribution function from Boltzmann's function takes into account the proper volume of the ions in the ionic atmosphere. This was also shown later by Eigen & Wicke (16), who, in addition, improved the original relation. The history of his relation has been repeatedly discussed (17 to 26). Wicke & Eigen (22, 27, 28) developed the field efficiently and extensively. Their earlier papers have been discussed in the preceding volume of this *Review* (4). The results of Bagchi, Dutta & Sengupta (14, 15, 25) are fundamentally in accord with the conclusions of Wicke and Eigen.

Perhaps somewhat surprising is the assumption of Wicke & Eigen that the mutual volume exclusion is to be taken into account only for ions of the same sign. The assumption is proposed for strongly hydrated ions but appears to have been generally used. It is assumed that the hydration shells are not penetrated in collisions of two ions of the same sign so that the full hydration volume is to be excluded. In the approach of a positive and a negative ion, however, the attractive force is considered to be strong enough for interpenetration so that only the proper volume of the hydrated ions is excluded. This volume can be neglected. A difficulty of this model appears to be that it is applied only to the ions in the ionic atmosphere. For the central ion, the classical model of the ionic radius is retained.

At present, the best support for the conclusions of Wicke & Eigen is furnished by the agreement which they find with experimental data. In recent papers, they discuss the thermodynamic properties at high concentrations (28, 29). Their object is a unified representation of activity coefficients, heat contents, heat capacities, volumes, and compressibilities. For several electrolytes such as the chlorides of lithium, magnesium, iron, and lanthanum they are successful in representing available data, using reasonable values for the ionic radius (5 to 6 Å) and no other empirical parameter. They conclude that these electrolytes are completely dissociated. Their conclusions regarding other electrolytes will be discussed in the section "Dissociation of strong electrolytes."

The distinction in the volume exclusion between ions of the same and opposite charge is not made by the Indian authors (cf. 25) nor by Falkenhagen & Schmutzer (30, 31). They represent the effect of the molal excluded proper volume v at the concentration c simply by subtracting log $(1-cv)$ from the Debye-Hückel term for log γ, treating v and the ionic radius as two independent empirical parameters. The agreement found for five salts is just about as good as one would expect for any reasonable function with two parameters. The statistics of the excluded proper volume has been recently discussed also by R. Schlögl (32).

Mixed electrolytes.—The free energy (thermodynamic potential) of a

solution is a single function that can be obtained by the determination of a single quantity (vapor pressure, e.m.f. and so on) over a composition range and appropriate integrations. All activity coefficients therefore can be derived from measurements of a single suitable quantity. Explicit relations have been derived only recently for the vapor pressure by McKay & Perring (33, 34) and for the e.m.f. by Argersinger (35), who uses earlier data as examples for the application. Robinson (36) applies the method of McKay & Perring to isopiestic data.

Growing interest in mixed electrolytes has led to renewed discussion of Brönsted's long neglected theory of specific interaction, which is as old as the theory of Debye and Hückel. Brönsted approximated the influence of short-range (nonelectrostatic) forces by taking into account the interaction of ions of opposite charge and neglecting the nonelectrostatic interaction of ions of the same charge. This plausible principle furnishes a simple, usually very good and useful approximation for moderately high concentrations. Scatchard & Breckenridge (37) use a power series in the ionic concentrations for representing short-range ionic interaction, and express and elucidate Brönsted's principle with the aid of the coefficients of the power series. Though extremely brief, their discussion expresses the principle perhaps better than Brönsted's original papers. They apply the principle to their isopiestic measurements of pure and mixed solutions of potassium and sodium phosphates and arsenates. A confirmation of Brönsted's theory for mixed solutions of weak acids and alkali salts is obtained by Ellilä (38) and Kilpi and co-workers (39).

Harned's rule, another useful approximation for activity coefficients in mixed electrolyte solutions, and an interesting thermodynamic corollary proposed by Glueckauf, McKay & Mathieson (40) have been tested by Robinson (41), Robinson & Lim (42), Jenkins & McKay (43), Harned (44), and Harned & Gary (45).

The discussion of electrolyte mixtures has been finally extended to heat contents and molal volumes by Young & Smith (46). They show that, as a first approximation, heat content and volume do not change if two solutions of equal ionic strength are mixed. Small deviations from this rule, appearing at high concentrations, are represented by an interaction term containing the ionic strength and the mole fractions of the two electrolytes on an electrolyte basis as factors. This term is similar to the excess free energy term of Scatchard and Hildebrand for mixtures of nonelectrolytes. Young and Smith also point out that their two approximations are related to Brönsted's principle and Harned's rule, respectively.

A systematic survey of thermodynamic relations, various approximations and experimental data in the field of mixtures appears to be overdue. A systematic and unified notation would also be desirable.

Coefficients of the limiting laws.—The numerical values of the coefficients appearing in the square-root relations for the logarithm of the activity coefficient, for heat content, molal volume and so on have been variously

discussed in recent years. For each of these properties it was, of course, necessary at first to show that the experimental and calculated limiting slopes agreed within the combined errors. This problem was solved some time ago.

Now the question is only the best representation, extrapolation, and use of available data. The best value of the limiting slope should be taken whether it be the "theoretical value" based on the theory of Debye and Hückel or the experimental value extrapolated from direct observations on several electrolytes.

Similar conclusions have been recently expressed by Guggenheim & Prue (47). The reliability of the "theoretical" coefficient for the logarithm of the activity coefficient has never been in doubt. The values used for aqueous solutions at 25° C. in more than twenty years differ by less than one per cent. The uncertainty of the "theoretical" coefficient for the heat content is only slightly higher, as a consequence of the influence of the temperature coefficient dD/dT of the dielectric constant D of water. The coefficient for the apparent molal heat capacity C_p of a uni-univalent electrolyte [9.0 ± 2 cal. kg.$^{0.5}$/° C. mole$^{1.5}$ (47); 9.194 cal. l.$^{0.5}$/° C. mole$^{1.5}$(48)] is much less precisely known because of the uncertainty of d^2D/dT^2. Guggenheim & Prue show in an analysis of the accurate data of Randall & Rossini (49, 49a) that the "theoretical" and experimental coefficients agree within the experimental errors. It may also be concluded that both are about equally uncertain.

Except for very minor differences [see (47) and (50)], there has been hardly any question regarding the application of the limiting laws. It is difficult to understand why some authors still use square-root relations with empirical coefficients derived from concentrated solutions. For example, the heat capacities of NaBr and KBr (51), $CoCl_2$, $NiCl_2$, $CuSO_4$, $BeSO_4$, and $AgNO_3$ (52) have been represented in this manner. The extrapolation to zero concentration would be obviously much better if the theoretical coefficient were used, if necessary with an additional term of higher order. This was pointed out for molal volumes long ago by one of the authors (53, 54), and recently also by Owen & Brinkley (55).

The value 1.86 ± 0.02 cm.^{3}l.$^{0.5}$/mole$^{0.5}$ for the limiting slope at 25° C. of the apparent molal volume of a uni-univalent electrolyte has been derived (54, 56) from the accurate density measurements of several observers. The mutual consistency of these data and the agreement with the "theoretical" value, based on Falckenberg's determination (57) of dD/dP, are very satisfactory. Kyropoulos' result (58) for dD/dP is incompatible with the density data, but the difference of about 20 per cent in dD/dP is within the limits of his experimental error. Owen & Brinkley [(55) see also (48, 59)], apparently not knowing the earlier discussions, derive the value of 2.517 for the coefficient of the apparent molal volume from Kyropoulos' result. New measurements of dD/dP by Harris, Haycock & Alder (60) are in quite satisfactory agreement with Falckenberg's result and the value 1.86. Any possibility of a doubt appears to be removed.

The accuracy attainable for densities is so high, and that for dD/dP so low, that the "theoretical" coefficient for the molal volume will hardly catch up with the experimental one. Still less favorable is the situation for the "theoretical" coefficients of the molal compressibility and expansibility, which depend on d^2D/dP^2 and $d^2D/dPdT$. Well-planned and fairly extensive determinations of compressibilities and expansibilities will lead to quite good values of the coefficients.

The encumbrance of calculations with complicated higher terms appears to be of doubtful value as long as the limiting coefficient is uncertain.

Conductivity.—Various attempts are made to develop and test relations containing terms beyond the limiting law of Debye and Onsager. Kraus and his co-workers (61, 62) analyze conductance data. Dye & Spedding (63) discuss the development of the electrophoretic term for unsymmetrical electrolytes and compare their results with conductances and transference numbers. Stokes (64) extended Onsager's theory in the application to diffusion.

The idea of accounting for the proper volume of the ions in the ionic atmosphere has been developed for conductivity by Falkenhagen and his co-workers (65, 66, 67). They also discuss the high voltage effect and diffusion. Stokes & Robinson (68, 69) develop and test relations for conductance which contain as parameters only the limiting conductance and an ionic radius independent of temperature. At several temperatures, they find good agreement with experimental conductances of uni-univalent electrolytes up to 0.02 *M* and with transference numbers up to 0.2 *M*. Wishaw & Stokes (70) follow Agar (71) in taking hydration into account in diffusion and conductance. They can fit the theoretical equations to their results up to 4 *M*. Adamson (72) compares theories of diffusion and concludes that present discrepancies between methods of measuring self-diffusion must be resolved before the test of the theories can be definitive.

Harned (73) and his co-workers have made extensive use of the conductometric method to determine accurately the diffusion coefficients of electrolytes in dilute aqueous solutions. Recent results are reported for CsCl (74), $MgCl_2$, $BaCl_2$ and $SrCl_2$ (75), all of which agree well with the theory of Onsager & Fuoss (76, 77) at concentrations below 0.01 *M*. In view of this agreement, the consistently low values observed by Harned & Levy (78) for $CaCl_2$ in the same concentration range are rather surprising. Using Gouy's optical method, Lyons & Riley (79) measured the diffusion coefficient of $CaCl_2$ at higher concentrations. They point out that the extrapolation of their data suggests that the results of Harned & Levy may be in error.

From an analysis of Harned & Hildreth's (80) diffusion data for NaCl, Guggenheim (81) concludes that the theory gives a more acccurate value for the mobility term than do the experimental data. For the diffusion coefficients of uni-univalent electrolytes, in fact, Harned (82) assumes the theoretical expression for the mobility term and thus calculates activity coefficients by integration of the observed diffusion coefficients over the concentration.

A good solution of the old problem of designing a conductivity cell for liquids of low conductivity is presented by Nichol & Fuoss (83). They eliminate stray electrical paths by using not only concentric cylindrical electrodes but also concentric leads.

Transference numbers.—In studying the moving-boundary method for the determination of transference numbers, Gordon & Kay (84) have shown experimentally that the concentration of the indicator ion approaches the Kohlrausch value close behind the moving boundary even though the initial concentration is lower. Subsequent work (85) indicated that the determination of this adjusted indicator concentration will provide a useful method for determining transference numbers. Muir, Graham & Gordon (86) succeeded in obtaining transference numbers by this method with a precision comparable to that of the customary moving-boundary method. In order to test the method, they worked with the system KCl–NaCl for which accurate transference data are available. They have developed a rather general method that can be used, in the absence of transference data, to determine the Kohlrausch ratio, which may then be extrapolated to zero concentration. The combination of this limiting ratio with the limiting equivalent conductances of the leading and indicator salts results in values for the ionic conductances.

Longsworth (87) presented a new variation of the moving-boundary technique for separating each of the ions in a mixture between two sharp boundaries by adding a leading and a trailing ion. The method might be useful for quantitative analysis or for the determination of transference numbers.

Measurements of transference numbers with the customary moving-boundary method have been reported for a number of rare earth ions in chloride, nitrate, and perchlorate solutions by Spedding and co-workers (63, 88). The transference numbers were found to vary linearly with the square root of the concentration in the range of measurements (below 0.1 *M*). Lang & King (89) determined the transference numbers of zinc and cadmium sulfates from the e.m.f. of concentration cells.

Molecular State

The dissociation of strong electrolytes.—The investigations of Gutowsky & Saika (90) and of Masuda & Kanda (91) show that the concentration dependence of nuclear magnetic resonance frequencies furnishes information on the dissociation of strong electrolytes. Some interesting results have been obtained and many more may be expected.

A magnetic field acting on a nucleus in a molecule is noticeably influenced by electrons and nuclei in its immediate vicinity, i.e., by the character of the adjoining bonds. The magnetic resonance frequency of a proton is therefore different in H_2O, H_3O^+, and HNO_3, the differences or "shifts" amounting to several millionths of the resonance frequency. Similar shifts for other nuclei, such as N or Cl, amount to several hundred-thousandths.

Such shifts can be measured with reasonable accuracy by the methods developed by Bloch and by Purcell and their co-workers. These shifts are only weakly influenced by the extramolecular environment of the nucleus in question; moreover, the influence is sufficiently approximated by means of the magnetic susceptibility.

In ionic equilibria a proton has only a short life time in each of the molecular species such as H_2O, H_3O^+, HNO_3, or $(HNO_3)_2$. In this case, only a single resonance frequency appears, which is the average of the frequencies for the various species, weighted according to concentrations. The variation of the measured frequency shift is therefore an indicator of the molecular composition of the solution.

The proton resonance shifts of acetic acid, HCl, HNO_3, $HClO_4$, H_2SO_4 NaOH, and KOH have been determined by Gutowski & Saika (90) at moderate concentrations. Hood, Redlich & Reilly (92) measured the proton shift of HNO_3 and $HClO_4$ in the whole concentration range and derived degrees of dissociation and dissociation constants. Masuda & Kanda (91, 93) determined the nitrogen shift of HNO_3 and the halogen shifts of $HClO_4$, HCl, HBr, and HI. The degrees of dissociation of HNO_3 (92) are in excellent agreement with values obtained by Young *et al.* (94) from the intensity of Raman lines. The dissociation constant $K = 22$ confirms the older value (95). The degrees of dissociation of $HClO_4$ (92, 93) are in good agreement with older determinations (96). The dissociation constant $K = 38$ has been derived (92) for $HClO_4$, the value $K = 1.8$ for CF_3COOH (97).

Nuclear magnetic resonance shares with optical properties, in particular the intensity of Raman lines, the decisive advantage of being insensitive to the environment of the molecule. The zone of confusion between undissociated molecules, ion pairs, and strongly interacting ions is narrow. A nucleus tells us fairly clearly whether it is in a molecule or in an ion, and disturbing influences are small.

Supersonic absorption and velocity dispersion is the basis of another method which has been developed in recent years and promises to be useful in the investigation of molecular changes in solutions. The method goes back to Einstein's work on the propagation of sound in dissociating gases (98). The anomalous absorption of $MgSO_4$ was first discovered in sea water and explained by incomplete dissociation by Liebermann (99). Several authors (99 to 105) studied the ultrasonic absorption of electrolytes, especially solutions of $MgSO_4$, and found interesting results. The important advantage of Eigen, Kurtze & Tamm (106 to 109) is the very large frequency range. Using five different methods, they covered the range from $5 \cdot 10^2$ to $3 \cdot 10^8$ c.p.s. They found no absorption by uni-univalent electrolytes. Uni-divalent and uni-trivalent electrolytes show absorption at high frequencies, increasing with the frequency. The dependence of the absorption of the sulfates of Mg, Co, Mn, Cu, Zn, Be, Al and of MgS_2O_3, $MgCrO_4$ on frequency and concentration indicates chemical reactions. For $MgSO_4$, most extensively investigated, the authors suggest both incomplete dissociation and hydrolysis.

Conductivity in a high field has become another useful method for investigating dissociation. Patterson and his co-workers have successfully developed and applied this method in recent years. They conclude (110, 111) that $MgSO_4$, $ZnSO_4$, and $CuSO_4$ are incompletely dissociated and find satisfactory agreement with the older dissociation constants 0.0063, 0.0049, and 0.0043, respectively, which go back to Davies and his co-workers. For $LaFe(CN)_6$ they find $K = 3.6 \cdot 10^{-4}$ (112).

As discussed in last year's *Annual Review of Physical Chemistry* (4), and mentioned in the section "Ionic interaction," Wicke & Eigen (28, 29) represented the thermodynamic properties of several salts up to fairly high concentrations by means of a single parameter, the ionic radius. They interpret the data for other salts as indicating incomplete dissociation and represent them with the aid of suitable values for the dissociation constant and heat of dissociation. Wicke and Eigen start from an appreciably stronger basis than previous authors who have also attempted to separate the effects of ionic interaction and incomplete dissociation on thermodynamic properties. Their advantage rests (*a*) on the use of a theoretically derived relation which represents interaction in a fairly wide concentration range with reasonable values of a single parameter; (*b*) on the representation of activity coefficients and thermal data by means of the same three parameters; and (*c*) for $MgSO_4$ also on the ultrasonic results. But their results are by no means altogether clear. It seems to be strange that the dissociation constants of NaCl and KBr should be as low as 6 and 2.5 moles/l., respectively, with no indication of undissociated molecules in the Raman or infrared spectrum of these and similar salts. A careful examination of the results of Wicke and Eigen, an extension of the method to other electrolytes and an attempt at checking dissociation data by independent methods appear to be very desirable. Calculations by the method of Wicke and Eigen for HNO_3, $HClO_4$, and $NaNO_3$ would lead to an interesting comparison with Raman results.

There is, of course, always the possibility of interpreting the dissociation constants of Wicke and Eigen as pertaining to "ion pairs" as introduced by Bjerrum. Such an interpretation would remove practically any possibility of a discrepancy between the results of different experimental methods. But it should be kept in mind that "ion pairs" are nothing more than a convenient model for representing higher terms of electrostatic interaction. On the other hand, real undissociated molecules are clearly demonstrated by well-interpreted Raman spectra. A distinction between "ion pairs" and undissociated molecules is possible and necessary.

It appears that ultrasonic absorption and high field conductivity are at present interpreted to indicate "ion pairs" rather than undissociated molecules. If this view is correct the results for $MgSO_4$, $ZnSO_4$, and $CuSO_4$ are not surprising but they lose significance since "ions pairs," after all, exist in all concentrated solutions of small ions.

In a careful examination, Woodward and his co-workers (113) concluded from the lack of a Raman line that TlOH is practically completely dissoci-

ated in aqueous solutions. But Bell & George (114) attempt to derive dissociation constants for TlOH, several thallium salts, and for $CaOH^+$ and $CaSO_4$ from determinations of the solubilities of $TlIO_3$ and $Ca(IO_3)_2$ in solutions of KOH and salts.

In aqueous periodic acid seven Raman lines have been found by Siebert (115). Four are the lines of IO_4^-, the other three are interpreted as the spectrum of H_5IO_6 to which Siebert assigns the spectrum of an octahedron. This interpretation is questionable for several reasons. Experience with other acids shows that OH and O are by no means vibrationally equivalent, the width of the lines does not support the interpretation, and a relation derived by Redlich, Kurz & Rosenfeld (116) from the central force model is not even approximately satisfied.

Concerning the dissociation constants of hydroxides, glycolates and lactates, derived from e.m.f.'s and conductances by Monk and his co-workers (117, 118, 119), it may be expected that the methods used furnish a good approximation for the weaker of the electrolytes investigated. The second dissociation constant of H_2SO_4 in aqueous methanol has been measured (e.m.f.) by Evans & Monk (120).

Posner (121) introduces the interesting assumption that the undissociated molecule HCl is a catalyst of the oxidation of ferrous ion by oxygen. Kortüm & Wilski (122) measure conductances of HCl and picric acid in aqueous ethanol and find that the deviation from the limiting law in the conductance of picric acid is not completely explained by incomplete dissociation. Somewhat similar results had been obtained earlier by Gross & Goldstern (123).

The ratio of the dissociation constants of MgF^+ and HF has been determined by Connick & Tsao (124), who used the interesting method of Brosset & Orring (125). The same method has been applied by Hepler, Kury & Hugus (126, 127) to the fluoride of indium and by Kury (128) to those of cerium, lanthanum, and gadolinium.

Spectrophotometric data for cerium chromate are presented by Tong & King (129). Brubaker (130) discusses the dissociation and hydrolysis of stannic sulfate on the basis of spectroscopic and migration data, but the possible influence of the formation of HSO_4^- should be taken into consideration.

Various ionic equilibria.—A wide variety of ionic equilibria has been studied. Optical properties and particularly Raman spectra furnish, as always, the safest information of the molecular state. Waters & Woodward (131) show, by means of a careful Raman study, that the ion Ag_2^{++} does not exist in aqueous solution in significant concentration, contrary to an assumption made by Davies & Morgan (132).

The Raman spectra of the chlorides, bromides and iodides of cadmium and mercury in aqueous solutions of alkali halides have been examined by Woodward and his co-workers (133) under such conditions that CdX_4^{--} and HgX_4^{--} are the only complex ions present in appreciable concentration.

Vanderzee & Dawson (134) derived equilibrium data for $CdCl^+$, $CdCl_2$, $CdCl_3^-$, and $CdCl_4^{--}$ from potentiometric measurements, and Erikson (135) obtained similar results for $CdCl_2$ and $CdBr_2$ by the polarographic method of Ringbom & Erikson (136). Ermolenko & Makkaveeva (137) study complexes in the system $CdCl_2$–KCl–H_2O. Accascina and co-workers (138, 139) confirm the complex formation of Cd^{++} in chloride solutions by determining the solubility of cadmium oxalate. Bailey & Patterson (140) find an effect of incomplete dissociation on high field conductivity. A critical survey of the Cd^{++} complex equilibria would be desirable.

Spectrophotometric information on the complexes of Cu^{++} with Cl^- and Br^- has been obtained by Kruh (141), on the hydrolysis of $SbCl_6^-$ in HCl solutions by Neumann (142). An interesting confirmation of the dimeric product $Fe_2(OH)_2^{++++}$ of the hydrolysis of Fe^{+++} has been derived from magnetic susceptibilities by Mulay & Selwood (143). The dimer is diamagnetic.

Work on the molecular state of anhydrous acids, so successful in recent years, continues. Fénéant-Eymard (144) presents a detailed Raman study of acetic acid and concludes that dimers exist not only in Hantzsch's form (two hydrogen bonds) but also in a form containing only a single hydrogen bond. A complex $HOAc \cdot HNO_3$ is found. Harris & Alder (145), too, conclude from dielectric measurements that a second form of the dimer exists but see the characteristic of the second form in a separation of the charges and consequently in a large dipole moment. The Raman spectra of mixtures of acetic and nitric acids have been determined also by Minc & Kecki (146).

The nitronium ion NO_2^+ is found in mixtures of HNO_3 with SO_3 but not with BF_3 by Gerding and his co-workers (147). The dissociation constants

$$BF_4^- = BF_3 + F^-; \quad K = 0.005$$
$$2HF = H_2F^+ + F^-; \quad K = 2.10^{-10}$$

have been derived from conductance (and vapor pressure) by Kilpatrick & Luborsky (148). Gillespie and his co-workers continue their successful work on conductance (149) and cryoscopy (150) in H_2SO_4. A review (151) includes the discussion of the dissociation of organic compounds in H_2SO_4. Wyatt (152) discusses the accuracy of cryoscopic measurements in H_2SO_4.

Polymerization of various ions has been studied: $Ti(SO_4)_2$ (153), peroxytitanic acid (154), CrO_4^{--} and $Cr_2O_7^{--}$ (155), and chromic, molybdic, and tungstic acids (156, 157). The equilibrium constant of the reaction $Al(OH)_3$ (hydrargillite) $+ OH^- = Al(OH)_4^-$ has been determined by Kuznetsov (158).

Density measurements are used by MacInnes & Dayhoff (159) for a determination of the equilibrium of I_3^- in methanol. The conductivity of iodine in pyridine leads, according to Kortüm & Wilski (160), to the dissociation constant of the iodine-pyridine complex. The conductivity of iodine solutions in hydrocarbons has been measured by Gindin (161). Griffiths (162) interprets conductances of $AgNO_3$ in aqueous and alcoholic solutions containing pyridine by means of a complex of Ag^+ and pyridine.

Burkin (163) believes that the conductance of coordination complexes of Cu and Pd in benzene can be explained by superposition of an "ion-pair" equilibrium and a true chemical dissociation equilibrium. Sadek & Fuoss (164) arrive at a similar explanation for the conductance of tetrabutylammonium bromide in mixtures of nitrobenzene and CCl_4.

The ionization of organic halides in nitroparaffin and nitroaromatic solutions has been derived from ultraviolet spectra by Evans and his co-workers (165, 166). Chu & Yu (167) found $K = 4.1 \cdot 10^{-4}$ (in mole fraction units) for the dissociation of diphenyl sodium

$$NaC_{12}H_{10} = Na^+ + C_{12}H_{10}^-$$

in tetrahydrofuran solution at 25°C. They found equal molar susceptibility for the anions of diphenyl, naphthalene, anthracene, phenanthrene, and *m*-terphenyl.

Weak electrolytes.—The measurement of high field conductivity furnishes interesting results for the true dissociation constants of such substances as H_2CO_3 and NH_4OH, investigated by Patterson and co-workers (168, 169). The same method was used for a determination of the acid dissociation constant of glycine (170) and for an investigation of the dissociation of $HgCl_2$ (171). Gusman & Cole (172) studied micelles in solutions of *n*-octadecyl pyridinium ions by measuring the high field conductivity.

Several authors (173, 174, 175) combine and compare potentiometric and spectrophotometric measurements in order to determine dissociation constants. Bates & Schwarzenbach (175) suggest the measurement of the activity of HCl in a cell without transference and the spectrophotometric measurement of the ratio B/HB of the concentrations of the base B and the ion HB. Denoting by c the concentration of Cl^-, they find that the quantity $K' = (a_{HCl}/c)(B/HB)$ is particularly suitable for the determination of the thermodynamic dissociation constant of HB by extrapolation to zero ionic strength. The advantage of K' can be easily recognized: It uses only well-defined measurable quantities and avoids pH and single activity coefficients.

The dissociation of UO_2F_2 and UO_2SO_4 (176), $CeSO_4^+$ (177), ten rare earth sulfates (178), HClO (179), FeS_2O_3 (180), $FePO_4$ (181), and calcium phosphates and citrates (182) has been studied. The first and second dissociation constants of H_3AsO_4 (183) and the third and fourth dissociation constants of ethylenediamine tetraacetic acid (184) have been measured.

Conductivity and dissociation of several inorganic salts in organic solvents have been determined. Accascina & Schiavo (185) find that $LiClO_4$, $NaClO_4$, and $KClO_4$ are weak electrolytes in acetone. Jones & Griswold (186) study alkali bromides, acetates and formates in acetic acid, Olson & Konecny (187) study LiBr in acetone.

Fulton & Swinehart (188) succeeded in deriving the first and second dissociation constants of zinc hydroxide by skillful use of their data for its solubility in HCl and NaOH. The solubility and hydrolysis of $Th(OH)_4$ presents a complicated problem which has been studied by Kraus & Holmberg

(189) and by Gayer & Leider (190). The hydrolysis of Fe^{++} (191), Al^{+++} (192), Sc^{+++} (193), and Tl^{+++} (194) has been studied.

Accurate measurements of heats of dilution of succinic acid are reported by Baumann (195). Approximately forty papers present data on the dissociation of organic substances.

Solvation.—The state of our knowledge of hydration, or, more correctly, a list of unsolved basic problems, was reviewed by Latimer (196). Some of these problems are the number of water molecules in the first layer, the energies and entropies of hydration. Taube (197) reviewed the information obtained regarding hydration by the determination of the O^{18} exchange rate and discussed the use of the distribution ratio of O^{18} between hydration water and solution water. Hydration energies and molal volumes of univalent ions in their relation to the theory of hydration are discussed by Passoth (198).

J. Bjerrum & Jörgensen (199) derive the constitution of aquo ions in alcoholic solution from spectroscopic evidence. Coordination numbers and hydration of uni- and divalent ions have been determined by Samoilov (200).

Lithium perchlorate is quite remarkable in being highly soluble in anhydrous ether but not in ether containing small amounts of water. Ekelin & Sillén (201) determined vapor pressure, activity coefficients, boiling points, conductance, density and molal volumes, and viscosity of these solutions. They compare their results and interpretation with extensive unpublished work by K. Fajans, O. Johnson and J. C. Chu.

A list of standard free energies, changes of heat content and entropy of hydration is given by Williams (202). Solvation energies are given by Attree (203).

Mattock (204) finds that the standard free energy of acid dissociation of an aquo ion (*e.g.*, $NaOH+H^+=Na^++H_2O$) and its heat of hydration are linearly related. Attempts at improving Born's equation for the energy of hydration (205) and oversimplified relations between activity coefficients and hydration (206, 207) may be registered.

A paper by Platzman & Franck (208) will probably influence future investigations. The authors point out that various properties of ionic solutions (density, compressibility, refractivity, transport properties and so on) somehow reflect the hydration of small ions "but in ways not yet clearly comprehended. Nevertheless, interpretations regarding the 'solvation' of ions have been freely advanced, leading to a literature which is notable for its enormous volume and for the utter chaos and ambiguity of its conclusions." The authors develop a model for the ultraviolet absorption of halide ions, calculating the transfer of an electron of the halide to an excited level determined by the resultant field of the halogen atom, the adjacent water molecules and the external polarized dielectric. They succeed in calculating the absorption frequencies of Cl^-, Br^-, and I^-, but the theory does not furnish any details regarding hydration.

Complex ions.—We are unable to discuss the numerous papers on complex

ions. Only a few papers will be mentioned which may be of more general interest.

J. Bjerrum's method of determining consecutive equilibrium constants has been critically discussed by Wormser (209), who recommends the comparison of results obtained by different methods (thermodynamic properties, light absorption, Raman spectra and so on) and the systematic comparison of similar complexes. Irving & Rossotti (210) suggest an improved method for calculating stability constants. Williams (211) summarizes heats and entropies of formation for 75 complex ions and discusses the factors which are believed to be principally controlling (charges, sizes, and electronegativities of the reactants, heats and entropies of hydration of reactants and products).

Numerous useful complexes with ethylenediamine tetraacetic acid have been investigated by several methods, namely, potentiometrically with the aid of cells without transference by Carini & Martell (212), polarographically by Schwarzenbach and co-workers (213), calorimetrically by Charles (214). The complexity constants of uranyl glycolates have been measured potentiometrically by Ahrland (215).

Thermodynamic Properties

Standard values.—Latimer (216) suggests a system of absolute standard entropies of ions, based on $\overline{S}° = -2.1$ cal./mole degree for H^+. On this basis a simple relation exists between hydration entropies and absolute free energies. He discusses the use of standard free energies and illustrates it for oxidation-reduction reactions of ions of U, Np, Pu, and Am (217). Powell (218) reviews the entropies of monoatomic ions and represents them with the aid of the absolute value Z of the charge and the radius r_e (Pauling radius + 1.3 Å) by means of $\overline{S}° = 47 - 154\ Z/r_e^2$ cal./degree·mole. The previously used term $1.5R \ln M$ containing the atomic weight M has been omitted as resulting from an error. The discrepancy between the observed relation and Born's equation is neither changed nor clarified. For oxyanions XO_n^{z-} a linear dependence of $\overline{S}°$ on Z and n is found by Connick & Powell (219). Similarly, a linear dependence of charge and number of ligands is found for complex ions by George, Hanania & Irvine (220). Simple relations for the differences of $\overline{S}°$, $\overline{H}°$, and $\overline{F}°$ of an ion in ammonia and in water are reported by Latimer & Jolly (221, 222).

Several authors examined the behavior and standard potential of various electrodes. Only the work on the electrode $Ag|AgCl, Cl^-$ will be mentioned here. A detailed survey of this and other silver–silver halide electrodes has been presented by Janz & Taniguchi (223). Guggenheim & Prue (224) revise the data for the standard potential $Ag|AgCl, Cl^-$. Bates & Bower (225) present new accurate measurements (also for the activity coefficients of HCl) between 0° and 90°C. Measurements in aqueous ethanol and isopropanol are reported by Harned & Allen (226), and in pure ethanol by Mukherjee (227).

Activity coefficients and heat contents.— The ultracentrifuge was previously

used for the determination of activity coefficients by Pedersen (228), and Drucker (229). Now Young, Kraus & Johnson have thoroughly developed the method. They derive the exact thermodynamic relations (230) and measure activity coefficients of CdI_2 and UO_2F_2 (231). The method, based on the balance between chemical and centrifugal potentials, furnishes results of satisfactory accuracy. The authors point out a complication that arises if two independent components of a solution react as, for instance, in hydrolysis. In this case the reaction product is distributed, in general, independently in the centrifuge so that it becomes a new independent component. Uranyl fluoride is largely dimerized in aqueous solution.

For the measurement of vapor pressures of dilute solutions, a new differential manometer is suggested by Brown & Delaney (232). By means of a flexible brass bellows and an attached strain gage, pressure differences of 10^{-6} mm. could be detected. The method should be useful if an accuracy that approaches the sensitivity could be attained. Stokes reports isopiestic measurements of $Ba(OAc)_2$, $Mg(OAc)_2$ (233), and $(NH_4)_2SO_4$ (234).

Nikolaev & Tananaev (235) determine the activity coefficients of the fluorides of K, Na, Li, NH_4 and several organic amines in anhydrous HF, using the cryoscopic and ebullioscopic methods. The concentration dependence indicates that salts diminish the association of the solvent as previously suggested by Getman and Daniels. Glauber salt, $Na_2SO_4 \cdot 10H_2O$, is used as a cryoscopic solvent for alkali chlorides, sulfates, nitrates, and HCl by Rolla & Cola (236).

A large number of investigations of activity coefficients, especially some in connection with ion exchange resins, cannot be discussed here. Of general interest, however, may be the observation made by Kraus & Nelson (237) that the logarithms of the activity coefficients of HCl in a resin and in water differ by a term proportional to the molality. The same result was found for $HAuCl_4$.

The representation of heat contents by a power series in the square root of the molality is briefly reviewed by Young & Smith (46). There exists a linear relationship between the coefficients of first and second order of the salts of a certain valence type. Moreover, the reciprocal of the first-order coefficient can be split into contributions of the constituent ions.

Salting out.—Theoretical discussions of the influence of electrolytes on the activity coefficients of nonelectrolytes have been presented by Shakhparonov (238) and by Nakajima (239). Long and his co-workers (240, 241) continued the systematic investigation of the salting-out effect and found in piperidine another polar electrolyte for which K^+ and Na^+ are reversed in the salting-out order. According to Waind (242), ethyl acetate is salted out by nitrates and salted in by perchlorates. The influence of uranyl and thorium salts on the miscibility of phenol and water has been studied by Bowden & Purnell (243).

Crockford (244) searched for a relation between the influence of organic solutes on the activity of HCl and on the dielectric constant of the solution.

According to a discussion remark by Scatchard, the effect may be roughly interpreted as due to hydration of the organic solute.

Acidity.—An excellent review of the old problem of the practical definition of the pH scale is presented by Hitchcock (245). Deno & Taft (246) believe that Hammett's acidity function can be sufficiently well approximated in the range 83 to 99.8 per cent H_2SO_4 by taking the second dissociation into account with the aid of a dissociation constant $K_2 = 50$ (in mole fractions). The acidity function of $HClO_4$ in nearly anhydrous and in aqueous acetic acid has been determined by Ludwig & Adams (247); the influence of salts on the acidity of HCl has been measured by Paul (248).

Phase boundaries, surfaces.—The osmotic pressure in the Donnan membrane equilibrium is discussed by Hill (249), the thermodynamics of cells with liquid-liquid junctions by Haase (250) and Bearman (251). Murphy (252) examines such cells in connection with an interesting study of equivalent impedance models for cells with solutions of nonuniform concentration. Teorell (253) succeeded in the analytical integration of the equations of motion for symmetric electrolytes. This work has been extended to unsymmetric electrolytes by H. Schlögl (254).

Overbeek (255) presents a valuable discussion of the concepts introduced in the investigation of electrochemical double layers and illustrates some of the basic relations by means of examples. Breyer & Gutmann (256) reexamine the Poisson-Boltzmann relation in the double layer problem. The proper volume of the ions of the ionic atmosphere is taken into account by Freise (257). A solution of the Poisson-Boltzmann equation for a spherical colloidal particle is presented by Hoskin (258).

Oel & Strehlow (259) measure the current integral on dipping an electrode into a solution and obtain a new confirmation of Billiter's value 0.475 v. of the "absolute" zero potential referred to the hydrogen electrode. Grahame (260) and Grahame & Soderberg (261) find that F^- and monoatomic cations are not chemisorbed on Hg. Electrocapillary curves are measured and related to hydration of the ions by McDonald (262) and by Darmois & Darmois (263). Parsons & Devanathan (264) measure electrocapillary curves in aqueous methanol solutions. Minc & Olezczyk (265) determine the e.m.f. between two copper electrodes, one of which is embedded in quartz sand with dilute $CuSO_4$ solutions as the electrolyte. The e.m.f. indicates the adsorption of the ion on the quartz. Caley & Stoffer (266) measure pH while adding $BaCl_2$ to K_2SO_4 and conversely, and find characteristic changes of pH ascribed to adsorption of H^+ or OH^- on the precipitates being formed. Ueda and his co-workers (267) produce an alternating voltage by applying sonic or supersonic vibrations to a capillary which is part of a galvanic cell. They attempt to utilize this observation for the study of interfacial structure.

Biochemical applications.—Scatchard and his co-workers (268) continue their thorough investigations of protein solutions. The osmotic pressure of solutions of albumin, globulin, and their mixtures in aqueous salt solutions at various concentrations, hydrogen ion concentrations, and temperatures has

been measured by means of an osmometer of the type introduced by Hepp (269). Electrostatic interaction in the mixed solutions at pH 6.3 is strong at low salt concentration and indicates a tendency for compound formation at high protein concentration. This was expected since the albumin carries a negative charge and the globulin a positive charge, each of about 12 equivalents per mole. The electrostatic concentration effect, however, is suppressed by a NaCl concentration as low as 0.03 *M*.

Shedlovsky (270) proposes the interesting hypothesis that proton transfer in bio-electrochemical reactions plays a role similar to electron transfer in ordinary electrodes. As a model, he investigates a cell containing solid lauric acid with a thin coat of barium laurate as "protode" and an aqueous solution of HCl and $BaCl_2$ as an electrolyte. The results substantiate the expected analogy between "protode" and electrode.

A somewhat related idea is proposed by Halla & Ruston (271). They measure the conductivity of aqueous solutions of humic acid as a function of pH. Their results indicate proton transfer within the micelle of the humic acid.

A model for biochemical ion exchange has been designed by Bonhoeffer, Kahlweit & Strehlow (272). They determine the e.m.f. of the cell

$$Hg_2Cl_2,\ LiCl(aq.,\ c_1)\ |\ \text{quinoline, quinine hydrochloride}\ |\ LiCl(aq.,\ c_2),\ HgCl_2.$$

It is in satisfactory agreement with the value calculated from partition coefficients, conductivities, and transference numbers of the solutes. Kahlweit & Strehlow (273) discuss the boundary potential of water-quinoline.

A series of papers by Hearon (274), Landahl (275), and Karreman (276, 277) describes investigations of nonstationary diffusion and membrane potentials in the presence of an additional (nonelectrolytic) force.

Fused salts.—Several authors measured electrode potentials in fused salts and activity coefficients by determining e.m.f.'s or melting temperatures. Petit (278), apparently not knowing earlier work (279) on the subject, points out that fused salts behave very much like perfect solutions.

Sutra (280) had previously found that the entropy of fusion of Ne, A, Kr, HCl, HI, and metals is roughly 3 cal./mole degree, corresponding to the formation of one hole per molecule. She observes now that the entropy of fusion of some binary salts is approximately 6 e.u., an elegant confirmation of the dissociation of fused salts.

Various Properties

Sonic and supersonic waves.—Some applications of the determination of supersonic absorption have been reviewed in the section "Dissociation of strong electrolytes." Barnartt (281) and Yeager & Hovorka (282) reviewed the investigation of electrolytes by means of sonic and supersonic waves. The most accurate values of the compressibility of solutions are obtained by measurement of the velocity of sound. Gucker & Haag (283) determined the apparent molal compressibilities of some amino acids and their isomeric

amides and presented a thorough discussion of molal compressibilites. Relative values of the limiting slopes for isomeric pairs do not agree with calculated values based upon the interactions of point dipoles in dielectric spheres [see Kirkwood (284)]. It may be true that the theoretical model is not an adequate representation of the zwitterion; but the test of the theory has not been rigorous because the data for dD/dP and $dD^2/dPdT$ are not accurate enough.

Barthel (285) has derived a new expression for the concentration dependence of sound velocity. Since the derivation introduces an empirical constant, the usefulness of the theory appears to be limited. His experimental results show that the velocity of sound decreases with increased concentration of $Pb(NO_3)_2$, uniquely in contrast to the behavior observed for other electrolytes. He suggests that the negative concentration dependence is due to the relatively great mass of the lead ion. From their studies of the pressure and temperature dependence of the velocity of sound in H_2O, Smith & Lawson (286) have concluded that water does not behave as "normal water" even at 10^4 atmospheres.

One aspect of interest in the study of hydration is the measurement of vibration potentials. In 1933, Debye (287) showed theoretically that a periodic potential related to the masses of the hydrated ions should exist in an electrolyte solution in a sonic field. Both of the previously mentioned review articles (281, 282) outline the development of the theory by numerous workers. Experimental realization of the theory by the actual determination of the primary hydration of ions is now imminent. Having developed a new pulse-modulated ultrasonic technique, Yeager, Dietrick & Hovorka (288) have obtained preliminary measurements of the vibration potential for dilute KCl solutions. Their results indicate a mass difference of approximately 80 atomic weight units between the hydrated potassium and chloride ions.

As an explanation for the linear decrease of the thermal conductivity of electrolyte solutions with concentration, Eigen (289) has proposed that heat is conducted through water by breaking and reforming of hydrogen bonds. The presence of an electrolyte prevents some water molecules—those involved in hydration of the ions—from taking part in the transfer of heat.

Viscosity.—Das (290) found that his measurements of the viscosity of dilute solutions of NH_4Cl and NH_4Br at 35°C. fit the equation of Jones and Dole in good agreement with the theory of viscosity of Dole and Falkenhagen.

For concentrated solutions, to which the theory is not applicable, a number of similar empirical equations have been reported. Ezrokhi (291) represented the viscosity of concentrated solutions of some of the individual salts of sea water by an expression of the form

$$\log \eta = Bc[1 - (ac)^n]$$

in which the c is the molar concentration and a and B are constants. The integer n is 2 for $MgCl_2$ and 1 for all of the other salts. Varlamov (292)

attempted to represent the available data on the viscosity of H_2SO_4 solutions by means of equations for four concentration ranges. Gopal (293) confirmed that the logarithm of the viscosity is nearly a linear function of $1/T$ for solutions of a number of salts, e.g., halides and nitrates of K and Ba.

Thermopotential.—Tyrrell (294) and Mazur (295) outline the thermodynamics of a thermocell consisting of a uniform electrolyte and two reversible electrodes which are equal but kept at different temperatures. Tyrrell shows a correlation between Ludwig-Soret coefficients and heats of dilution. He suggests that the Ludwig-Soret coefficients represent a measure of the interaction between the hydrated ions and the solvent. Tyrrell & Colledge (296) relate the e.m.f. of the thermocell to the Ludwig-Soret coefficient of the electrolyte and discuss pairs of electrolytes with common ions. The theory is derived for dilute solutions, but their experimental results for moderately concentrated solutions are in qualitative accord with it. Tanner (297) investigates Ludwig-Soret coefficients and the rate with which thermal diffusion approaches equilibrium. Murin & Popov (298) measure Ludwig-Soret coefficients of electrolytes. Baranowski & Demichowicz (299) devise a new thermal diffusion tube. They heat the electrolyte in a capillary internally by means of alternating current and cool the wall of the capillary. Results with $CuSO_4$ are in agreement with de Groot's theoretical discussion.

Dewald & Lepoutre (300) derive from measurements of the thermoelectric power a confirmation of the model of a degenerate electron gas for concentrated solutions of Na and K in NH_3.

Optical properties.—For aqueous solutions of the hydrohalic acids and halide salts, Sivaramakrishnan (301) finds deviations from Becquerel's relationship between dispersion and Faraday's effect. He ascribes the deviations to the existence of H_3O^+ and to hydration of ions. Randall & Taylor (302) report an anomalous concentration dependence of Faraday's effect in electrolyte solutions. Further investigations would be desirable.

Dielectric properties.—Gaümann & Günthard (303) observed that the dielectric constants of several amino acids in water–methanol and water–dioxane solvents increase linearly with concentration. They were able to fit their experimental results with a simple model of a spherical dipole surrounded by a concentric solvate sphere that has a greater polarization than does the bulk solvent. New measurements of the dielectric constant of trifluoroacetic acid by Harris & O'Konski (304) have shown that this compound does not exhibit the anomalous dielectric behavior previously reported (305).

Fifteen years ago Hammett (306) suggested that the constancy of activity coefficients of electrolytes in concentrated H_2SO_4 was caused by the lack of ionic interaction in a medium with a high dielectric constant. Actual measurements of the dielectric constant have finally been made by Brand, James & Rutherford (307) who observed a value of 110 at 20°C. This is much too low to satisfy Hammett's suggestion. Brand, James & Rutherford contend that the activity coefficients could appear to be constant, however, because (*a*) experimental difficulties reduce the accuracy sufficiently; (*b*) the narrow

range of concentration and the high ionic strength (0.05 to 0.20) resulting from the autoprotolysis or its repression by added water restrict the limits of variation; and (*c*) the common anion HSO_4^- has a leveling effect.

Ionic Reaction Rates

There are two particular aspects that should be reviewed, namely, the extremely high rate of ionic reactions and the specific influence of the electric charge. During half a century ionic reaction rates were outside the range of any conceivable investigation. Only recently several independent and promising methods have been proposed.

Rates of fast reactions.—The resolution and shape of magnetic resonance lines furnish an elegant means of finding short lifetimes of molecular species. Essentially, the method is based on Heisenberg's principle. If the difference of the magnetic resonance frequencies of two states is of the same order of magnitude as the reciprocal lifetimes, the resonance lines merge. If the difference is larger, one observes two distinct lines.

A mean lifetime of $1.2 \cdot 10^{-6}$ sec. is derived for the naphthalene anion from the electron magnetic resonance spectrum of a tetrahydrofuran solution of naphthalene and naphthalene salt by Ward & Weissman (308). Proton magnetic resonance has been used by Zimmerman (309) for determining the lifetime of V^{++++} complexes. Ogg (310) finds a triplet for the proton resonance spectrum of dry liquid NH_3, but only one line in the presence of water, which makes rapid exchange of the protons possible. The rate of exchange of a proton between NH_3 and NH_2^- (KNH_2 or $NaNH_2$ in liquid NH_3) is found to be $4.6 \cdot 10^8$ l./mole sec.

The determination of ionic reaction rates by the measurement of anomalous supersonic absorption has been discussed by Freedman (311), Manes (312), and Eigen (313). The order of magnitude 10^{10}–10^{11} l./mole sec. is found by Eigen for reactions involving H^+ or OH^- with an ion of opposite charge.

Eigen and also Pearson (314) suggest the use of high frequency-high voltage fields as a method for determining ionic reaction rates.

Isotope exchange.—The rate of isotopic exchange, in itself an interesting problem, can be used, as shown especially by Taube, for the solution of various kinetic problems. Aten & Bigot (315) studied F exchange between H_2SiF_6 and HF; Lee (316) did not find Cl exchange between ClO_3^- and ClO_4^-; van der Straaten (317) found Cl exchange between green $CrCl_3$ and Cl^-; Sullivan and his co-workers (318) examined the charge transfer between Np(IV) and Np(V). The O exchange between water and $CrCl_3$ was studied in detail by Mackenzie & Miller (319). Taube's review (197) has been mentioned before. Posey & Taube (320) studied O exchange of complex Co ions.

Electron transfer.—Taube and his co-workers (321, 322) conclude from radioactive tracer experiments that a charge transfer between two ions of the same sign,

$$Cr^{++} + Fe^{+++} = Cr^{+++} + Fe^{++}$$

or in the similar reaction between Fe^{++} and Fe^{+++}, proceeds through an activated complex such as

$$CrXFe^{++++}$$

containing a negative ion X^-. These results are in agreement with theoretical discussions of Platzman & Franck (208) who point out that ions of the same sign cannot readily penetrate their hydration shells so that the rate of direct reaction cannot be appreciable.

Various kinetic results.—Anbar & Taube (323) use isotopic oxygen exchange to establish a mechanism for the reaction of nitrite and H_2O_2 involving pernitrous acid HOONO and the ion NO^+ as intermediates. A mechanism involving the ion NO^+ was suggested earlier by Abel (324). He also proposed (325) a comprehensive mechanism for the reaction of NH_4^+ (or amines) and HNO_2, a reaction inconclusively discussed by Anbar and Taube.

Gerischer (326) analyzes the discharge mechanism of Zn^{++} and complex zinc ions by measuring the polarization impedance as a function of the frequency. Harty & Rollefson (327) and Svirbely & Sharpless (328) determine the influence of ions on the quenching of the fluorescence of quinine, fluorescein and eosin.

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SOLUTIONS OF NONELECTROLYTES[1]

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Gaseous Solutions

The *PVT* relationships for gaseous mixtures, like those for pure gases, depend on the sizes and shapes of the molecules and on the mutual forces between them. Theoretical and experimental work dealing with this dependence has been reviewed by Rowlinson (1) and by Hirschfelder, Curtiss & Bird (2).

Rowlinson, Sumner & Sutton (3) have derived approximate expressions for calculation of the second and third virial coefficients of a binary gaseous mixture from constants for the components, for cases for which certain parameters, pertaining to the three types of molecular pairs, are nearly alike. Pople (4) and Rowlinson (5) have dealt with the forces between nonspherical molecules and the effect of their shape on the properties of gases and liquids. Rice & Hirschfelder (6) have computed the second virial coefficient as a function of the parameters of a potential equation containing an inverse sixth-power attraction term and an exponential repulsion term. Mason (7) has used this equation to evaluate collision integrals. Mason & Rice (8), with these relationships and experimental virial coefficients and viscosity data for pure He and pure H_2, have computed virial coefficients, viscosities, and thermal diffusion factors for their mixtures.

Shepp & Bauer (9) have shown how to compute the entropy increments in gaseous bimolecular addition reactions from structural and spectroscopic characteristics of the molecules. Slutsky & Bauer (10) have applied this procedure to carboxylic acid vapors, in which dimerization occurs, and to mixtures produced by the addition of F_2 to a halogen fluoride, in which addition occurs to give ClF_3, etc.

Lambert, Murphy & Sanday (11) have dealt with binary mixtures of polar and nonpolar gases, assuming partial association. Fair agreement was obtained with experimental second virial coefficients for mixtures of cyclohexane with diethylamine, acetonitrile, and acetone. Atack & Rice (12), from *PVT* data for gaseous mixtures of iodine and benzene, have calculated the equilibrium constant for association to $C_6H_6 \cdot I_2$.

Schäfer & Moesta (13) have used diffusion and viscosity data for A—He, A—N_2, and N_2—H_2 mixtures to study collision cross sections and intermolecular forces. Lee & Wilke (14) have measured diffusion coefficients for 11 binary gaseous systems. Thacker & Rowlinson (15) have measured viscosities of mixtures of polar gases in seven binary systems and related the results to thermodynamic properties of the corresponding liquid solutions. They conclude that the effect of polar and other noncentral forces on the

[1] The survey of the literature pertaining to this review was completed in January, 1955.

thermodynamic properties of the liquid solutions is greater than on the viscosities of the gases. Assuming a Lennard-Jones potential, Cohen, Offerhaus & de Boer (16) have made a theoretical calculation of diffusion coefficients, viscosity, heat conductivity, thermal diffusion ratio, and second virial coefficient for gaseous He^3—He^4 mixtures. Becker, Misenta & Schmeissner (17) have measured the viscosity of such mixtures, as a function of composition, at 2.6 and 4.2°K.

McGrath & Ubbelohde (18) have studied by ultrasonic methods the efficiency of intermolecular collisions in the interconversion of translational and vibrational energy, for gaseous mixtures of ethylene with eight other gases. They conclude that molecular flexibility is an important factor in promoting energy transfer.

The theory of thermal diffusion in gaseous mixtures has been extended by Srivastava & Srivastava (19) to take account of the variation of the diffusion constant with temperature. Hirota & Sasaki (20) have made thermal diffusion measurements on N_2—H_2 mixtures and shown that they can be interpreted on the basis of the Lennard-Jones potential, except for very high H_2 concentrations.

Liquid Solutions: Thermodynamic Properties

Various theoretical treatments (21, 22) during recent years have led to the following expression for the partial molal free energy of mixing and the activity of a component of a binary liquid solution, in terms of the partial molal volumes ($\bar{V}_1$, $\bar{V}_2$) and the volume fractions ($\underline{V}_1$, $\underline{V}_2$):

$$\Delta\bar{F}_1/RT \equiv \ln a_1 = \ln \underline{V}_1 + (1 - \bar{V}_1/\bar{V}_2)\underline{V}_2 + \mu\underline{V}_2^2 \qquad 1$$

μ is a function, characteristic of the solvent-solute pair, which approaches constancy as $\underline{V}_2$ approaches zero. It consists of an entropy part, μ_s, and a heat content part, μ_h. Assuming the former to be negligible, Hildebrand (23) has related μ to "solubility parameters" (δ_1, δ_2) by the semiempirical equation

$$\mu = (\bar{V}_1/RT)(\delta_1 - \delta_2)^2 \qquad 2$$

where δ_1 and δ_2 are the square roots of the energies of vaporization per cc. Although the use of these solubility parameters involves the neglect of μ_s and of any variation of μ_h with concentration, as well as other approximations, they have proven very useful guides to solubility behavior.

The writer (24) has recently discussed, in some detail, the factors affecting μ_s and μ_h and their variation with concentration. He (25) has also published a new theoretical approach to property-structure relationships, applicable to special types of condensed systems. Many properties are approximately additively deducible from the numbers and properties of the "structons" present, a structon consisting of an atom (or group of atoms or molecule) surrounded by close neighbors in a given way. The types and numbers of structons in a solid or liquid of given composition at equilibrium

depend on their relative stabilities and on geometric and stoichiometric factors. The theory has so far been applied primarily to glasses, but it is also applicable to many liquid solutions. It should be possible to develop a quantitative treatment of their thermodynamic (and many other) properties, considering structons, rather than molecules, as components.

Reik & Gebert (26) have derived equations for the thermodynamic properties of the components of a solution in terms of the coefficients in the virial expansion of the osmotic pressure and their temperature derivatives. Katti & Bhagat (27) have discussed the configurational energy of regular solutions as a function of the coefficient of expansion. Boissonnas & Noordtzij (28) have derived an equation for the heat of mixing of the components of a binary solution, as a function of the a priori probabilities of the three kinds of intermolecular contacts and the related energies. Rehage & Jenckel (29) have proposed that the second derivative of the excess free energy of mixing, with respect to the mole fraction of the solute, be used as a measure of the goodness of a solvent.

Barker & Smith (30) have interpreted thermodynamic data on chloroform-benzene, chloroform-acetone, ethanol-chloroform, ethanol-acetone, and ethanol-ether solutions with the aid of Barker's theory of intermolecular association at specific contact points. Plewes, Jardine & Butler (31), finding only small heats of mixing for binary solutions of water with methanol, ethanol, and *n*-propanol, have attributed the considerable deviations from ideality to differences in the molecular sizes. Adcock & McGlashan (32) measured heats of mixing of benzene in solutions of biphenyl in benzene, finding agreement with equations derived from the lattice model in dilute solutions, but not at higher concentrations. They also measured heats of mixing in CCl_4—$CHCl_3$ and CCl_4—C_6H_{12} solutions. Brandt (33) has reported heats of mixing for *n*-hexane-methylcyclohexane and *n*-decane-*trans*-decalin solutions. Thacker & Rowlinson (34) have measured heats and volumes of mixing for six binary systems, having acetone, isopropanol, isopropylamine, and propionitrile as components, also for the ethanol-acetonitrile system. Large negative heats and volumes of mixing in the isopropanol-isopropylamine system indicate strong hydrogen bonding between unlike molecules.

In qualitative agreement with theoretical predictions by Prigogine & Bellemans (35), solutions of molecules of nearly equal sizes but very different molecular force fields have been found by Mathot & Desmyter (36), Thacker & Rowlinson (37) and Meares (38) to exhibit positive heats of mixing but negative volume changes on mixing. Kohler & Rott (39) studied volume changes on mixing, at 15° and 25°C., for three binary solutions, in each of which the two components have nearly equal molar volumes. Only partial agreement with Prigogine's theory (35) was found.

Kretschmer & Wiebe (40) have modified the Redlich & Kister (41) theory of the thermodynamic properties of solutions with associated components by using Equation 1 for the free energy and by expressing the

equilibrium constant in terms of moles per unit volume. Satisfactory agreement was obtained with experimental data on vapor pressures and energies and entropies of mixing for binary solutions of an alcohol with an aliphatic hydrocarbon, on the assumption that the alcohol molecules associate to form polymers of all orders. For ethanol-toluene solutions it was necessary to assume that each alcohol monomer or polymer can combine with one molecule of hydrocarbon.

Griffiths (42) has published partial molal volume curves for the methanol-water, dioxane-ethanol, pyridine-ethanol, pyridine-water, acetone-water, and dioxane-water systems. The methanol-water and dioxane-water curves. like those for the ethanol-water system (43), show sharp breaks. The reviewer suggests that these occur at compositions at which the set of structon types (25) present suddenly changes.

Markgraf & Nikuradse (44) measured the volume change on mixing for 29 binary systems of organic molecules, relating their results qualitatively to intermolecular forces. Hydrogen bond formation between the two species produces large contractions. For solutions of simple chlorine compounds with the same second component, the volume change effect always follows the order: CH_2Cl_2, CCl_4, $CHCl_3$, $CCl_2{=}CHCl$. The first gives the greatest volume change, if it is positive, and the least, if negative.

Masterton (45) found that the partial molal volumes of methane, ethane, propane, and benzene in water solution are less than in nonpolar solvents, presumably because of the relatively high internal pressure of water. Except for benzene, the temperature coefficient of the partial molal volume decreases with rising temperature. This is interpreted as due to the breaking up of a cagelike ("iceberg") structure of the water surrounding the aliphatic molecules [Claussen & Polglase (46)].

For the methanol-(butyl sebacate) system, Colmant (47) has measured vapor pressures, densities, refractive indices, viscosities, and dielectric constants and has calculated the composition-dependence of the thermodynamic properties. Assuming the departures from the measured entropies of mixing from the theoretical values on which Equation 1 was based to be due only to association of the alcohol, he has computed values of the average degree of association as a function of the concentration. A value of about two was obtained at the limit, pure methanol. Since departures from the simple entropy equation may be due to various other causes (24), these calculated degrees of association should be considered merely tentative. Colmant also found proportionality between the molal volume of the solution and the activity coefficient of the methanol, over a considerable composition range. Curves of the logarithm of the (activity coefficient/molar volume) ratio versus the volume fraction consist chiefly of linear segments, with rather sharp breaks. This looks like another suitable system for the application of structon theory (25).

Davies & Jones (48) have evaluated heats of solution and heats of solvation for benzoic, salicylic, *p*-hydroxybenzoic, and *o*-methoxybenzoic acids

in benzene and CCl_4 solutions and have discussed the intermolecular energies involved. Davies & Griffiths (49) have studied the acetic acid monomer-dimer equilibrium in benzene and water solutions, using cryoscopic and distribution methods.

Activity-concentration relationships, deduced from liquid-vapor equilibrium measurements, have been published for the following systems: water-ethanol and water-propanol-1 [Hansen & Miller (50)]; water-glycolamide [Stokes (51)]; benzene-cyclohexane and benzene-aniline [Kortüm & Freier (52)]; and (carbon tetrachloride)-chloroform [McGlashan, Prue & Sainsbury (53)].

Densities and refractive indices (n_D) have been reported for the BrF_3—BrF_5 system by Stein, Vogel & Ludewig (54). Stein & Vogel (55) have also published refractive indices for the UF_6—BrF_3 and UF_6—BrF_5 systems.

Young, Kraus & Johnson (56) have derived an equation for the ratio of the activities of a substance at two concentrations, in a binary solution at equilibrium in an ultracentrifuge. They have applied this equation to aqueous solutions of cadmium iodide and uranyl fluoride (57).

Dave & Dewar (58) have investigated binary systems in which one component can form a nematic liquid-crystal phase and the other not. In all solutions studied the liquid phase is a homogeneous single phase; it may or may not be anisotropic.

Early work on He^3—He^4 solutions and mixtures has been summarized by London (59). Nanda (60) has pointed out that previous theories differ greatly in regard to their predictions of the temperature-dependence of the heat of mixing. New theories have been presented during the past year by Goldstein (61) and Rice (62). The latter's theory agrees reasonably well with recently published heat and entropy of mixing data.

Thermodynamic data for the following liquid binary alloy systems have been published: Ag, with Cd, In, Sn, and Sb, at 450°C. [Kleppa (63)]; Zn—In, at 427°C. [Svirbely (64)]; Pb—Bi, at 640°C. [Gonser (65)]; and Cu—Cd, at 602°C. [Riccoboni *et al.* (66)].

Hook, Letaw & Gropp (67) have reported polarographic studies of three organic compounds (benzalacetone, benzophenone, fluorenone), as well as some inorganic substances, in formamide-acetamide mixtures.

Liquid-Liquid Equilibria

Francis (68) has reported the mutual solubilities of liquid CO_2 with 261 other substances, at temperatures between 21 and 26°C. and equilibrium pressures, approaching 65 atm. Density measurements on solutions of CO_2 in acetic acid, benzene, methanol, and *n*-heptane showed contractions of 10 to 15 per cent. Solubility relationships for 464 ternary systems were published as triangular graphs. Carbon dioxide at moderate concentrations has a strong homogenizing action upon pairs of other liquids, but at high concentrations it exhibits a precipitating action.

Cox (69) has studied the miscibility with water of six alkyl derivatives of

pyridine. All show solubility curves of the closed loop type. Andon, Cox & Herington (70) found that the logarithms of the activity coefficients of pyridine and its alkyl derivatives in very dilute aqueous solution, are additive functions of the groups making up the molecule. There is no indication that the structures of the pyridine base solutions are exceptional.

Armstrong & Rotariu (71) have found that gallium dissolves slightly in liquid yellow phosphorus at 45°C.

Liquid-liquid equilibrium studies, showing the composition limits for separation into two liquid phases, have been published on the following systems: ozone-oxygen [Jenkins & Birdsall (72)]; bromine-(bromine trifluoride) [Fischer, Steunenberg & Vogel (73)]; ethanol-*n*-heptane-water [Schweppe & Lorah (74)]; 1-butanol-(methyl 1-butyl ketone)-water, 1-butyraldehyde-(ethyl acetate)-water and 1-hexane-methylethylketone-water [Jones & McCants (75)]; (*tert*-butyl alcohol)-(*tert*-butyl hypochlorite)-water [Westwater & Audrieth (76)]; benzene-*n*-heptane-(diethylene glycol) [Johnson & Francis (77)]; ethylbenzene-diacetonealcohol-water and styrene-diacetonealcohol-water [Crooke & Van Winkle (78)]; (acetic acid)-water, with 1-butanol, methylethylketone, furfural, cyclohexanol, and nitromethane [Skrzec & Murphy (79)]; methanol-aniline-benzene-water [Francis (80)]; and sulfur-β-naphthylamine-diphenylamine [Krupatkin (81)].

Alders (82) has found that, for a given homologous series of compounds (excluding the lowest members) and a given pair of immiscible solvents, the logarithm of the distribution coefficient varies rectilinearly with the number of carbon atoms: $\log K_0 = a - bn$. For a given solvent pair, b has the same value for all series. Bhat, Lu & Johnson (83) have studied the distribution, between water and carbon tetrachloride, of acetic, *n*-propionic, *n*-butyric, and *n*-valeric acids at 20, 25, and 30°C. Hollingsworth, Taber & Daubert (84) have described a method for finding the composition of a 3-component liquid system which will give the best separation of two of the components.

The critical temperature for mutual solubility has been shown to be almost a rectilinear function of the mole fraction for the acetone-chloroform system [Swietoslawski & Kreglewski (85)] and for systems of pyridine with isopropyl, isobutyl, and isoamyl alcohols [Kreglewski (86)]. Atack & Rice (87) have presented new evidence that the coexistence curve for a binary mixture showing incomplete miscibility has a finite horizontal top, in the cyclohexane-aniline system. Hildebrand *et al.* (88) have measured the effect of high centrifugal fields upon the critical temperature for separation of a liquid system into two phases, for the systems: (*n*-perfluoroheptane)-(2,2,4-trimethylpentane) and perfluoromethylcyclohexane-(carbon tetrachloride). After subtracting the hydrostatic pressure effect, a rise of 1.9° (under the conditions of the experiments) was observed in the first case; this was attributed to a sedimentation effect arising from the large density difference between the components. In the other case the densities are nearly the same and no significant residual effect was observed.

Dauphin (89) has pointed out the usefulness of a "universal diagram,"

based on equations of van Laar, in which two constants (A, B), characteristic of the components and the temperature, are plotted, one against the other. The compositions of the two liquid phases can be determined from A and B, also the reverse, and composition changes resulting from a temperature change can be predicted.

Liquid-Gas Equilibria

The solubilities of the inert gases in water have been measured over a temperature range by Morrison & Johnstone (90). From these measurements and others previously published on aqueous paraffin solutions, they concluded that the heat of solution at 4° is almost a rectilinear function of the molecular polarizability, for nonpolar gases having polarizabilities as large as that of argon. At higher temperatures the inert gas behavior differs from that of the hydrocarbons. Gjaldbaek & Andersen (91) have measured solubilities of N_2, O_2, CO_2, and CO in 12 polar solvents. Departures from Hildebrand's solubility parameter relationship (Eqs. 1 and 2) are roughly proportional to the dipole moments of the solvents.

Friedman (92) has determined the molal heat and entropy of solution of SF_6 in water to be -7 kcal. and -50 entropy units, respectively. This entropy of solution is about 10 entropy units more negative than normal, hence the water molecules around each solute molecule must be more regularly arranged than is usually the case [cf. Frank & Evans (93)]. Friedman also measured the solubilities of SF_6, OsO_4, and the inert gases in nitromethane, obtaining rough agreement with solubility parameter theory (Eqs. 1 and 2). The solubilities of the inert gases in a variety of solvents obeyed the equation $\log x_2 = a_1 + b_1 g_2$, where a_1 and b_1 depend only on the solvent and g_2 depends only on the solute.

Hildebrand (94) has found that the equation $\log c_2 = a_2 + b_2\delta_1$ holds for a variety of solutions of gases in liquids. Here, c_2 is the solubility at 25° C. and 1 atm., a_2 and b_2 are constants for a given solute, and δ_1 is the solubility parameter of the solvent.

The solubilities of He, Ne, A, and Kr in 13 hydrocarbon solvents have been measured at three temperatures by Clever *et al.* (95). For the aliphatic solvents ΔH and ΔS for the solution process are practically independent of the solvent. Ridenour, Weatherford & Capell (96) have measured solubilities of N_2, O_2, A, CO_2, and CH_4 in molten waxes.

Edwards *et al.* (97) have described a method of using vapor-liquid equilibrium data for binary systems to predict the equilibrium relationships for related multicomponent systems. They have applied this method to the benzene-chloroform-acetone, water-ethanol-methanol and phenol-toluene-methylcyclohexane-isooctane systems.

Norrish & Twigg (98) have published and tested, for 25 binary systems, an equation relating the mole fractions (x_1, x_2, y_1, y_2) in the liquid and gaseous states to the ratio (K) of the molar heats of vaporization:

$$Z \equiv \ln(y_1 x_2^K / x_1 y_2^K) = M x_1 + C.$$

M and C are constants for a given system at a given total pressure, related to the heats of vaporization and the boiling points of the pure substances. The only systems tested which did not give linear Z versus x_1 plots were those containing water.

Kuhn (99) has developed a theory of separation of the components of azeotropic solutions, assuming that they are regular or nearly so.

Benson, Allen & Copeland (100) have found empirically that, for many nonazeotropic binary systems in the neighborhood of the critical locus, the isotherms obey a simple "rectilinear diameter law," relating the mole fractions in the two phases and the vapor pressures.

Nycander & Gabrielson (101) have reported boiling temperatures and compositions of the azeotropes in the systems: acetaldehyde-(ethyl ether), (propylene oxide)- (ethyl ether), and (ethylene glycol)-(diethylene glycol monoethyl ether). Zieborak & Markowska-Majewska (102) have reported a liquid-vapor equilibrium study of various ternary systems involving naphthalene, cresols, and pyridine bases, which form minimum-boiling azeotropes.

Other liquid-gas equilibrium studies have been published during the year on the following systems: argon-oxygen [Clark, Din & Robb (103)]; methane-propane [Akers, Burns & Fairchild (104)]; (carbon dioxide)-propane [Akers, Kelley & Lipscomb (105)]; nitrogen-*n*-heptane [Akers, Kehn & Kilgore (106)]; nitrogen-*n*-butane [Akers, Attwell & Robinson (107)]; H_2O—D_2O [Combs, Googin & Smith (108)]; $C^{12}O$—$C^{13}O$ and $C^{12}H_4$—$C^{13}H_4$ [Groth, Ihle & Murrenhoff (109)]; oxygen-water [Truesdale & Downing (110)]; phosphine-water [Weston (111)]; (nitric acid)-(nitrogen dioxide) [Corcoran, Reamer & Sage (112)]; hydrogen-ethylene, hydrogen-ethane, hydrogen-propylene and hydrogen-propane [Williams & Katz (113)]; heptane-toluene and methanol-(carbon tetrachloride) [Hipkin & Myers (114)]; α-pinene-β-pinene [Tucker & Hawkins (115)]; naphthalene-1-octadecene [Martin & Van Winkle (116)]; naphthalene-*n*-tetradecane [Haynes & Van Winkle (117)]; naphthalene-1-hexadecene, *n*-tetradecane-1-hexadecene, and naphthalene-*n*-tetradecane-1-hexadecene [Ward & Van Winkle (118)]; ethylbenzene-styrene [White & Van Winkle (119)]; acetaldehyde-water [Dobrinskaya, Markovich & Neiman (120)]; pyridine-water [Ibl, Dandliker & Trumpler (121)]; formaldehyde-water [Iliceto (122)]; (diacetone alcohol)-water [Hack & Van Winkle (123)]; acetone-chloroform and acetone-benzene [Tallmadge & Canjar (124)]; *m*- and *p*-xylenes in 39 solvents [Chu *et al.* (125)]; formaldehyde-methanol-water [Green & Vener (126)]; (propionic acid)-*n*-octane-water [Johnson, Furter & Barry (127)]; (boron trifluoride)-benzene and (boron trifluoride)-toluene [Wheeler & Keating (128)]; and (boron trifluoride)-ammonia and (boron trifluoride)-dimethylamine [Brown & Johnson (129)].

Solid-Liquid Equilibria

On the basis of Eq. 1, the equilibrium concentration (expressed as volume

fraction, V_2), for equilibrium between a solid and its solution in a liquid, is related to the heat of fusion of the solute (ΔH_f) and its melting point (T_m) by the equation

$$\ln V_2 + (1 - \overline{V}_2/\overline{V}_1)V_1 + (\overline{V}_2/\overline{V}_1)\mu V_1^2 = -\frac{\Delta H_f}{R}\left(\frac{T_m - T}{TT_m}\right). \qquad 3$$

(If the difference between the specific heats of solid and liquid solute is not negligible, another term, proportional to that difference, must be included.) This relationship, usually in combination with Eq. 2, has been much used in theoretical discussions of equilibrium between a solid and its solution in a liquid.

From the approximately rectilinear dependence of the heat of fusion and the molal volume on n, the number of CH_2 units, the approximate equation, $\log x_2 = a + bn$, is readily deduced (130, 131) for the solubilities of compounds in an homologous series at a given temperature. Because of this, as Skau & Boucher (132) have pointed out, graphs of $\log x_2$ versus n are useful for interpolation to obtain the solubilities of missing members.

McLaughlin & Scott (133) have measured the solubilities of iodine, stannic iodide, and phenanthrene in perfluoro-tri-*n*-butylamine and perfluoro-*n*-propylpyrane. Discussing their results, as well as those of Rotariu, Hanrahan & Fruin (134) on perfluoro-tri-*n*-butylamine solutions with methylcyclohexane, *n*-hexane, and isooctane, together with earlier work on solutions of fluorochemicals, they conclude that for most—but not all—such solutions, the regular solution theory (Eqs. 1 and 2) is applicable, provided one uses solubility parameters for the fluorine compounds which are somewhat lower than those deduced from energies of vaporization. For mixtures of fluorochemicals with compounds containing hydrocarbon groups, there are still discrepancies. They present arguments against Simons' (135, 136) hypothesis of abnormally great interpenetration between adjacent hydrocarbon molecules, also against Hildebrand's (137) proposal that the solubility parameters of hydrocarbons be arbitrarily increased. They do not, however, have any satisfactory explanation of their own to offer for the remaining anomalies. A more detailed theoretical analysis of these solutions, involving consideration of the dependence (24) of μ_h and μ_s on structure and concentration, is obviously needed.

Adamsky & Wheeler (138) have made cryoscopic and solubility studies of binary systems of boron bromide with aluminum bromide, stannic bromide, arsenic bromide, and stannic iodide. No evidence of compound formation was found.

Somayajulu & Palit (139) have shown that anthracene exhibits cosolvency in binary mixtures of iodobenzene or iodoethane with benzene, cyclohexane, or cyclohexene. They attribute this to strong complex formation tendencies of the iodides.

Ross (140) has concluded, from a study of the (freezing point)-composition curves of aqueous solutions of 11 alkyl hydroxy compounds, that they all

associate with water or form hydrates. The freezing points are higher or lower than normal, depending on whether the ratio of carbon atoms to hydroxyl groups is greater or less than two.

Kudryavtseva & Krutikova (141) have published solubility-composition diagrams for ternary systems of ϵ-caprolactam and water with dichlorethane, chloroform, and methylene chloride. Giguère & Secco (142) have determined the solid-liquid phase diagram for the D_2O—D_2O_2 system, comparing it with that for the H_2O—H_2O_2 system. Penkala (143), studying the solid-liquid phase diagram for binary systems of one component and a series of homologues, found a gradual transition from an ideal eutectic type to a solid solution type, with unlimited solubility. The eutectics all lie on a single curve.

Smirnov (144) has made cryoscopic studies of naphthalene solutions of iodine and mercuric chloride and of iodine and mercuric iodide. In the former case he concludes that complexes are formed, probably of all of the following compositions: $4HgCl_2 \cdot I_2$; $3HgCl_2 \cdot I_2$; $HgCl_2 \cdot I_2$; $HgCl_2 \cdot 2I_2$. In the latter system, polyiodides are not formed, but the HgI_2 molecules associate, if the iodine is added to the naphthalene before the mercuric iodide.

Dionisyev & Dzhelomanova (145) have studied solutions of 8-hydroxyquinoline in organic acids, using melting point, viscosity, and electrical conductivity methods. They conclude that compounds are formed with acetic, monochloracetic, benzoic, salicylic, and *p*-nitrobenzoic acids, but not with *p*-hydroxybenzoic, cinnamic, or hydroxycinnamic acids. Kirillova & Dionisyev (146) have made a similar study of compound formation in solutions of quinoline in nitrophenols and naphthols.

Bousquet & Dodé (147) have derived an equation for determining the heat of fusion of one constituent of a regular binary solution from that of the other and the fusion diagram of the mixture. Mathieu (148) has described a method of determining the total amount of impurities in a liquid from the departure from a constant rate of fusion. Samples as small as 0.5 gm. suffice.

Fischer & Vogel have determined the solid-liquid phase diagrams for the UF_6—BrF_3, UF_6—BrF_5 (149) and UF_6—Br_2 (150) systems. All three are of the simple eutectic type. Svirbely & Selis (151) have redetermined the diagram for gallium-indium alloys, by means of specific resistance measurements.

Ermolenko & Lemets (152) have reported an inverse relationship between adsorption of nitro-, chloro- and hydroxy-benzoic acids, onto charcoal from solutions in mixed organic solvents, and their solubility. The nature of the substituent group has a larger effect on solubility and adsorption than does the position of the group (*o*-, *m*-, *p*-). Polarity and H···· bond formation are important.

Spectrum Studies

Ioffe & Lilich (153), studying the benzene-tetranitromethane system, concluded from spectrum changes that unstable complexes are formed.

Their concentration must be very low, however, since melting point, viscosity, surface tension, and refractive index data gave no indication of chemical interaction. Nikuradse & Ulbrich (154) interpret the increase in the C—H valence frequency of chloroform, on solution in solvents containing strongly polar groups, as due to the breaking of the weak intermolecular H···· bonds existing in pure chloroform. Josien & Lascombe (155), in an infrared study of acetone in 16 solvents, found that in polar solvents the fractional shift of the C=O valence frequency shows a closer proportionality with the refractive index ratio, $(n^2-1)/(2n^2+1)$, than with the dielectric constant ratio, $(\epsilon-1)/(2\epsilon+1)$. They conclude that in such solvents molecular associations are more effective in lowering the frequency than is polarization by orientation.

Harris & Hobbs (156) have used infrared absorption measurements to study the dimerization of acetic, the three chloroacetic and benzoic acids in CCl_4 solutions. Barrow & Yerger (157) have similarly studied the dimerization of acetic acid in CCl_4 and $CHCl_3$. For the chloroform solutions they deduced the equilibrium constant for the formation of a 1:1 complex. Brown & Mathieson (158), using data on the partition of the chloroacetic acids between water and organic solvents, have deduced equilibrium constants for the distribution between the solvents and for dimerization in the organic solvents. Differences in behavior in different solvents can be explained in terms of H···· bonding between the different types of molecules.

Josien & Fuson (159) have reported that the shift of the N—H stretching frequency in the infrared spectrum of pyrrole, on dissolving it in nonpolar solvents, varies with dielectric constant according to the relationship deduced by Kirkwood (160) and Bauer & Magat (161). Deviations in polar solvents are attributed to H···· bonding and the formation of complexes. Chiorboli & Manaresi (162) have investigated the Raman spectra of solutions of pyrrole in benzene, pyridine, ethanol, dioxane, and acetone. Association, presumably to a 1:1 complex, was indicated in pyridine solution, but not in the others.

The near ultraviolet spectra of pyridine, the isomeric picolines, 2- and 3-fluoropyridine, 2- and 3-chloropyridine, and 2- and 3-bromopyridine in isooctane and ethanol solutions have been studied by Stephenson (163). In the ethanol solutions, H···· bonding is indicated, between the OH group and the pyridine nitrogen. Hydrogen bonding seems to be absent in the solutions of the compounds with substituents in the 2-positions.

From a study of phenol solutions in cyclohexane and carbon tetrachloride, von Keussler (164) concluded that monomeric phenol and polymers produced by H···· bond association are simultaneously present.

Barrow & Yerger (165) have made an infrared study of the formation of H···· bond complexes between triethylamine and chloroform in their mutual solutions and in solutions of both in CCl_4, also between triethylamine and ethanol in CCl_4 solution. For solutions of triethylamine and acetic acid in CCl_4 and $CHCl_3$, they (166) have identified the association and reaction products and computed the equilibrium constants.

Klemperer *et al.* (167) have studied the infrared spectra of N-ethylacetamide, N-*n*-butylacetamide, and γ-butyrolactam in CCl_4 solution, also N-ethylacetamide in various solvents. They attribute the observed differences primarily to variation of the constant for H---- bond polymerization. There is weak H---- bonding between chloroform and the carbonyl group of the amide. The conclusions of Mizushima *et al.* (168), that secondary amides form several H---- bond polymers while lactams form only dimers, are supported.

Infrared spectra of five phosphorus compounds (triphenyl phosphine, triphenyl phosphate, triphenyl phosphite, tributyl phosphate, and triphenyl phosphine oxide) in various organic solvents have been studied by Geddes (169). The results were interpreted as evidence for H---- bonding between hydroxyl and phosphoryl groups and dipolar interaction between phenyl and carbonyl groups.

From a study of the visible and ultraviolet spectra of anhydrous and aqueous organic solutions of uranyl complexes with β-diketones, Sacconi & Giannoni (170) have concluded that there are strong, essentially covalent, bonds connecting the organic ligands to the uranium, also that the complexes are solvated and hydrated to a high degree.

Bayliss & McRae (171) have extended the former's theory of the shifts in the electronic spectra of organic molecules when they are dissolved in a liquid. Superimposed on a general "polarization red shift," due to solvent polarization by the transition dipole, they assume shifts due to the fact that the solute molecule, when excited, is (by the Franck-Condon principle) initially in a state of strain with respect to its environment. The magnitude of the strain and its effect on the absorption frequency can be related to the polarity of solvent and solute, changes in dipole moment and dimensions of the solute molecule during the transition, and other factors. These authors (172) have measured the ultraviolet absorption spectra of acetone, crotonaldehyde, nitromethane, and nitrobenzene in both nonpolar and polar solvents, interpreting the observations in terms of their theory.

Ham (173) has studied the visible and ultraviolet spectra of solutions of iodine in various organic compounds, in organic glasses at liquid nitrogen temperatures. He interprets his results on the basis of the formation of charge-transfer complexes, rejecting Bayliss' theory, chiefly because it offers no obvious explanation of the 1:1 nature of the complexes and because it would seem to require a considerable shift in the visible spectrum of iodine in heptane solution at high pressures, whereas no shift was observed (174). The spectrum changes found depend both on the concentration of the electron donor molecule and on the glass composition.

Reid & Mulliken (175), from the visible and ultraviolet spectra of dilute solutions of iodine plus pyridine in heptane, have computed the changes in heat content, entropy, and free energy associated with the formation of a 1:1 complex. Dallinga (176), from x-ray diffraction data on solutions of iodine in benzene, mesitylene, and pyridine, has concluded that the shortest C----I

distances in the first two are 3.93 and 3.84 Å, respectively. A 2.90 Å distance found for the pyridine solutions might be due to the presence of some I_3^-.

Although the visible and ultraviolet spectra of I_2 are greatly shifted on solution in alkyl iodides, Schuler (177) found no major alterations in the infrared spectrum of the alkyl iodide solvents. Haller, Jura & Pimentel (178) have made an infrared study of changes in the spectra of benzene, toluene, mesitylene, hexamethylbenzene, naphthalene, cyclohexane, and methylcyclohexane, resulting from the addition of iodine. Except in the case of naphthalene, changes were noted and attributed either to weak complex formation or strong solvent perturbations.

Katzin & Katz (179) have observed that solutions of iodine in liquid hydrogen fluoride are violet, but that the absorption maximum is shifted markedly in HF-(diethyl ether) and HF-methanol solutions. They conclude that the HF interacts but little with iodine, but competes with iodine for electron donor molecules.

A spectrophotometric study of the visible and ultraviolet spectra of iodine chloride in various solvents has been carried out by Buckles & Mills (180). The equilibrium constant for the formation of a 1:1 complex with propionitrile was estimated to be 153. For this and other cases of such complexes the absorption maximum is shifted from about 460 mμ to about 350 mμ.

The transfer of excitation energy between unlike molecules in liquid solutions has been the subject of a number of researches. Bowen & Livingston (181) have concluded that the energy transfer is a result of a bimolecular reaction between the excited molecule and a normal, to-be-excited, molecule. The rate is not determined by diffusion, nor by the rate of formation of dimers. Moodie & Reid (182) concluded that the transfer follows the formation of a complex. Lampe & Noyes (183) found the quantum yield to be greatly diminished as the molecular weight of the solvent increases. Burton & Patrick (184), studying the radiolysis of a mixture of cyclohexane and benzene-d_6 by 1.5 Mv. electrons, found that excited cyclohexane is protected from decomposition by the benzene-d_6, the mechanism being energy transfer. Mixtures of propionaldehyde and benzene-d_6 were also studied. Cohen & Weinreb (185) have observed energy transfer in many organic solutions, when excited by λ2537.

Nonequilibrium Properties

Lamm (186) has published a formal theory of diffusion and its relation to self-diffusion, sedimentation equilibrium, and viscosity. Ogston (187) has compared the thermodynamic and kinetic expressions for diffusion in binary liquid systems, with particular attention to the statistical basis for the latter and to the expression of nonideal behavior. Krichevskiĭ, Khazanova & Linshits (188) have reported that diffusion, in the phenol-water system, falls nearly to zero in the critical region. Sandquist & Lyons (189) have measured diffusion coefficients (D), viscosities (η), densities, and molar refractive in-

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crements for solutions of biphenyl in benzene. Plots of $D\eta/T$ versus concentration at 25° and 35°C. are identical, within experimental error.

Grunberg (190) has shown that theoretical viscosity equations can be used to compute an interchange energy, $w_{visc.}$ Values of this quantity were computed for benzene-cyclohexane, CCl_4-cyclohexane and CCl_4-benzene solutions, also for five binary solutions involving *cis*- and *trans*-decalin, tetralin, benzene, and CCl_4. This interchange energy is considerably greater than that derived from activity data.

Wirtz (191) has pointed out that the interchange of nearest neighbors and viscous processes in the environment both contribute to the velocity of migration of molecules in liquids. Because of this, Stokes' law and Riecke's law can be expected to be valid only in limiting cases.

A theory of thermal diffusion in liquid mixtures has been presented by Rutherford & Drickamer (192). Experimental thermal diffusion studies have been reported for the following sets of binary solutions: six from CCl_4, CCl_3CH_3, $CCl_2(CH_3)_2$, and $C(CH_3)_4$ [Jeener & Thomaes (193)]; six from CCl_4, CBr_4, $C_2H_2Cl_4$, $C_2H_2Br_4$, $C_2H_4Cl_2$, and $C_2H_4Br_2$ [Saxton, Dougherty & Drickamer (194)]; CS_2 with *n*-hexane, *n*-heptane and *n*-octane [Rutherford & Drickamer (195)]; $C_2H_2Cl_4$ with normal paraffins, having $n = 6$, 7, 8, 9, 14, and 18 [Saxton & Drickamer (196)]; CS_2 with five isomeric hexanes [Rutherford, Dougherty & Drickamer (197)].

Dielectric absorption measurements can be used to deduce relaxation times for solute molecules in liquid solutions. Theory and experiments in this field have been summarized by Davies (198).

Kadaba (199) has measured the loss factor of the microwave dielectric constant for (phenyl isothiocyanate)-diethylamine solutions, finding a sharp minimum at the 1:1 concentration, corresponding to a very high and sharp maximum in the viscosity curve (200). The reviewer suggests that the data indicate the formation of linear polymeric (H····· bonded?) complexes, probably having the general formula $(AB)_nA$ on one side of the 1:1 composition and $B(AB)_n$ on the other.

Joerges-Heyden, Nikuradse & Ulbrich (201) have applied Kirkwood's (202) theory of the dielectric polarization of polar liquids to solutions of organic compounds, for which no strong associations between like molecules would be expected.

Pryor & Roscoe (203) have interpreted measurements of the velocity of sound in aqueous sugar solutions as showing that the sugar molecules have "solvation envelopes" of attached water molecules.

The viscosities of liquid sodium-potassium alloys up to 700°C. have been measured by Ewing, Grand & Miller (204).

Solid Solutions

No attempt is made here to deal with the structure of alloys or other solid solutions. Those interested in the structure of alloys may be referred

to the recent book by Hume-Rothery & Raynor (205). The theory of the electronic structure of alloys has been dealt with by Friedel (206).

Prigogine, Bingen & Jeener (207, 208) have discussed theoretically the zero-point energy of solid isotopic mixtures. Varley (209) has presented a theoretical treatment of the heats of formation of binary alloys, based on the assumption that the "free" electrons are in two sets of energy levels, associated with the two kinds of atoms. Fair agreement with experiment is obtained for alloys in which the two elements are not far apart in the periodic table.

Lieser & Witte (210) have studied the solubility of hydrogen in Mg—Cu—Zn alloys.

Surface Solutions

Theoretically and experimentally, Elton (211) has found that the surface activity coefficients of the components of a binary perfect solution, at the liquid-air interface, vary linearly with the mole fractions in the solution.

Briegleb & Scholze (212) have studied the adsorption of acetone and chloroform from a mixture of their vapors onto small glass spheres of uniform size. Blackburn & Kipling (213) have studied the effect of H····· bonding on adsorption by charcoal from binary mixtures of miscible liquids. Normally, the adsorption is confined almost entirely to a monolayer, but strong H····· bonding sometimes leads to secondary adsorption onto the first layer. Lloyd & Harris (214) have studied adsorption onto active carbon, silica gel, and clay from toluene-isooctane solutions. Singleton & Halsey (215) have measured adsorption isotherms of argon on preadsorbed xenon and krypton films on graphitized carbon black at 77°K. The A—Kr films consist of an approximately regular solution.

Macromolecular Solutions

Papers pertaining particularly to solutions of high polymers and other macromolecules have been omitted from this survey, since they are dealt with elsewhere in this volume (see chapter on Polymerization Kinetics, pages 359 to 380).

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THE SOLID STATE: DIFFUSION IN METALS AND ALLOYS[1]

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During the past few years there has been an impressive activity in the field of solid state diffusion, and particularly so in metallic diffusion. As a result, recent comprehensive reviews are, in part, already out of date [Jost (1); Le Claire (2, 3)].

Late research in the diffusion field has, in large measure, been sparked by three important independent developments: (*a*) The ready availability of radioactive isotopes of a large number of chemical elements. (*b*) The discovery of new experimental methods. Among these the internal friction technique pioneered by Zener and co-workers has proved particularly important (4). Another promising development is the use of nuclear magnetic resonance techniques for the study of self-diffusion in solids [See e.g., Gutowsky & McGarvey (5)]. (*c*) The discovery in 1942 by Kirkendall (6) of the movement of fiducial markers placed at the original diffusion interface in conventional alloy diffusion couples. The marker movement, which indicates that the interdiffusion process is associated with a flow of mass, has led to a critical review of the whole problem of interdiffusion in metals.

These three key developments have been paired with important growth in related fields. It is sufficient to mention such things as the more general availability of metals in a high state of purity, improved techniques in the preparation of single crystals, recognition of the importance of grain-boundaries, etc.

In virtually all investigations of solid-state diffusion carried out up to the present time it has been found that the experimental diffusion coefficient D may be represented by a simple Arrhenius type equation

$$D = D_o \exp(-H/RT)$$

where D_o and H are constants, while R and T have their usual meaning. This suggests that the diffusion rate is determined by a single thermally activated process. It is worth noting that both D_o and H have been found in very careful investigations to be essentially independent of temperature [see e.g., Sonder, Slifkin & Tomizuka (7)]. Possible exceptions to this rule are found in studies of diffusion in silver-zinc alloys by Nowick (8), and in work on the diffusion of interstitial oxygen and nitrogen in tantalum and niobium by Marx, Baker & Sivertsen (9). In both cases an internal friction technique was used. However, most apparent exceptions from Arrhenius's law have been explained by assuming that the observed diffusion process is the result of two or more separate diffusion mechanisms operating simultaneously. A

[1] The survey of literature pertaining to this review was completed in December, 1954.

typical example is offered by the simultaneous grain-boundary and lattice diffusion in polycrystalline solids [Hoffman & Turnbull (10)].

Interdiffusion in Substitutional Alloys

Phenomenological theory.—The classical experiments in solid-state diffusion consisted of the bringing together of two solid specimens of uniform but different composition through a plane interface. When the temperature was raised, interdiffusion occurred in the direction normal to the interface. After the lapse of some time the concentration-penetration curve was determined along the diffusion direction. The results of such experiments were derived from application of Fick's 1st and 2nd laws, which for uni-directional diffusion are ordinarily written

$$J = -D(\partial c/\partial x) \qquad \text{I.}$$

and

$$(\partial c/\partial t) = \partial(D\partial c/\partial x)/\partial x \qquad \text{II.}$$

Here J is the flux, c is concentration (g. atoms/cc.), while D is the diffusion coefficient or diffusivity defined through Fick's 1st law. It has long been recognized that the diffusion coefficient may be a function of composition, temperature, pressure and, if the considered specimen is not a single crystal, also to some extent of the past history of the specimen. The standard literature on diffusion in solids gives information on various experimental arrangements suitable for determination of D from the concentration-penetration curve. Since about 1930 a wealth of experimental information on interdiffusion in metal systems has been evaluated by a straightforward use of these methods. Most commonly it has been assumed that Fick's 2nd law may be applied, and the data have been evaluated by means of the well-known Boltzmann-Matano analysis, with D assumed to be a single-valued function of composition (11).

In recent years, however, it has become recognized that the driving force in diffusion is not simply the concentration gradient, but more generally a gradient of the thermodynamic potentials. The most general equations expressing the relation between the flux of component i and these driving forces are the Onsager-Fuoss relations, originally stated for irreversible transport phenomena in electrolytic solutions (12).

$$J_i = -\sum_{k=1}^{s} \Omega_{ik} \operatorname{grad} \mu_k' \quad (i = 1, 2, \cdots, s) \qquad \text{III.}$$

The thermodynamic potential μ' occurring in this equation is the sum of the Gibbs potential μ and $z_i e\psi$, where $z_i e$ is the charge on the ion i and ψ is the local electrostatic field. According to Onsager's principle of microscopic reversibility the coefficients appearing in equation III form a symmetric matrix: $\Omega_{ik} = \Omega_{ki}$, for all i, k. For simplicity we consider all electrostatic forces to be absent, and diffusion to occur in one dimension only. Then

$$J_i = -\sum \Omega_{ik}(\partial \mu_k/\partial x) \qquad \text{IV.}$$

It has been customary in discussions of diffusion in the solid state to assume that the migration of one species is independent of the migration of the other species present. Under these conditions we have $\Omega_{ik} = O$, for $i \neq k$. However, it has been pointed out, e.g., by Bardeen & Herring (13), that this assumption is questionable, and that the cross-terms may be important even in the simplest types of diffusion experiments (see below). At the present time, we shall tacitly assume that the cross-terms may be neglected, and that equation IV may be written in the simple form

$$J_i = -\Omega_i(\partial\mu_i/\partial x) \qquad \text{V.}$$

The conventionally defined "intrinsic" or "partial" diffusion coefficient for component i then equals

$$D_i = \Omega_i(\partial\mu_i/\partial c_i)_{P,T} \qquad \text{VIa.}$$

In the special case when the considered solution is ideal we get the familiar Einstein relation,

$$c_iD_i = \Omega_iRT, \qquad \text{VIb.}$$

which relates mobilities (Ω_i/c_i) to diffusion coefficients. This relation is of particular importance when mobilities may be determined independent of the usual diffusion methods, as in the case of charged ions in ionic solids and in impurity semiconductors.

In the general case equation VI may be rewritten in terms of the activity coefficient, f_i

$$c_iD_i = \Omega_iRT[1 + c_i(\partial \ln f_i/\partial c_i)] \qquad \text{VII.}$$

From equations VI and VII Darken (14) derived a relation between the "chemical" or interdiffusion coefficient D_i for component i defined by equation VII, and the self-diffusion coefficient D_i^+, for diffusion of a radioactive tracer of the species i in a solid or the same composition. Apart from an isotope effect the mobilities may be assumed to be the same for interdiffusion and for tracer diffusion. With Darken we get

$$D_i = D_i^+[1 + c_i(\partial \ln f_i/\partial c_i)] \qquad \text{VIII.}$$

If a binary diffusion system is considered, we shall have two equations of this type, one for each component. If we may assume that the Gibbs-Duhem relation is valid in the diffusion zone, we get simply $D_1/D_1^+ = D_2/D_2^+$. For a system of this type Darken also derived the following relation between the conventional diffusion coefficient, D, derived from interdiffusion experiments, and the two intrinsic coefficients, D_1 and D_2.

$$D = N_2D_1 + N_1D_2 \qquad \text{IX.}$$

Here N_1 and N_2 are the mole fractions of the two components. If we combine equations VIII and IX, make use of the Gibbs-Duhem relation, and replace concentrations with mole fractions, we obtain

$$D = (D_1^+N_2 + D_2^+N_1)[1 + N_1(\partial \ln f_1/\partial N_1)]. \qquad \text{X.}$$

Darken was able to test this relation by available diffusion data for a gold-

silver alloy [Johnson (15)], and found that the relation was well satisfied.

However, a classical interdiffusion experiment which yields a value of D, does not give us enough information to evaluate the two intrinsic diffusivities D_1 and D_2. According to Darken's phenomenological theory, the required additional information is provided by the afore-mentioned interface shift discovered by Kirkendall.

The Kirkendall effect.—Kirkendall, and later Smigelskas & Kirkendall (16), observed that in the diffusion of copper—α-brass diffusion couples, there was a small but marked shift of the original diffusion interface in the direction toward the zinc-rich side. Kirkendall suggested that the shift results from the zinc atoms having a larger diffusivity than the copper atoms.

It has been found that the marker shift, x_m, is proportional to the square root of the diffusion time. Assuming that the changes in lattice parameter can be neglected, and that the lattice is maintained intact in the diffusion zone and offers the diffusing particles a constant cross-section, Darken (14) derives an expression which related the observed marker shift to the difference between the two intrinsic diffusivities

$$\partial x_m/\partial t = (D_2 - D_1)(\partial N_2/\partial x) \equiv (D_1 - D_2)(\partial N_1/\partial x) \qquad \text{XI.}$$

From this relation it is, in principle, possible to derive values for the intrinsic diffusivities from a classical interdiffusion experiment combined with a measurement of the marker shift.

The first quantitative test of this part of Darken's theory was offered by Seith & Kottmann (17), who repeated Johnson's interdiffusion experiment on gold-silver alloys, now observing the marker shift. They found excellent agreement between the values D_{Ag} and D_{Au} obtained by the two independent methods.

However, this agreement does not carry as much weight as is apparent. This is due to the fact that the assumptions on which Darken's derivation is based will hardly ever be satisfied in practical diffusion experiments. In addition to possible changes in lattice parameter, one frequently finds that there is an over-all volume change associated with the diffusion process and that porosity develops in the diffusion zone.

There have been various attempts to refine Darken's theory by taking into account possible changes in lattice parameter and volume. This has been achieved by introducing a more suitable parameter for the diffusion path. Da Silva & Mehl (18) propose to measure the diffusion length in terms of the number of lattice planes, thus automatically correcting for the change in lattice parameter. Hartley & Crank (19), who, independent of Darken, derived an analogous set of relations, suggest that concentrations should be measured wholly in terms of mole fractions. They go on to define a linear coordinate in terms of the third root of the gram atomic volume. This suggestion, which was originally advanced for diffusion in polymer systems was adopted for alloy diffusion by Wagner (20), and more recently by Cohen, Wagner & Reynolds (21). A modification of the Matano procedure for systems exhibiting volume changes has also been suggested by Prager (22).

The observations of Kirkendall on the shift of the diffusion interface in substitutional diffusion experiments have now been confirmed by a number of independent investigators. Until very recently these observations were restricted to face-centered cubic (f.c.c.) structures, but work by Landergren & Mehl (23) on diffusion in β-brass and by Shewmon (24) on the titanium—molybdenum system have now confirmed that the effect is found also in body-centered cubic (b.c.c.) structures.

A particularly comprehensive study of the Kirkendall effect was carried out by Da Silva & Mehl (18) who explored the phenomenon in a series of binary alloy systems (Cu—Zn, Cu—Al, Cu—Sn, Cu—Ni, Ag—Au, and Cu—Au), using several different types of marker materials and a variety of temperatures. They found that for any one type of diffusion couple and temperature, different types of markers all move at the same rate. Their work confirmed that marker displacement is proportional to the square root of time, thus indicating that the shift is a genuine diffusion controlled process. They further noted that dimensional changes in the specimens appeared to be restricted to the direction of the diffusion flow. However, they reported that only a small or negligible amount of porosity developed in the samples, and on this point more recent investigators have arrived at different conclusions. Thus, Bückle & Blin (25) found porosity on the alloy side of copper—α-brass and copper—α-CuAl couples, while work by Barnes (26) (Cu—Zn, Cu—Ni); by Balluffi & Alexander (27) (Cu—Zn, Cu—Ni, Ag—Au); by Seith & Kottmann (17) (Ag—Au, Ag—Pd, Au—Ni, Cu—Ni, Ni—Co); by Heumann & Kottmann (28) (Co—Ni, Fe—Ni); by Fitzer (29) (Fe—Si); by Seith & Ludwig (30, 31) (Cu—Ni); and by Balluffi & Seigle (32) (Cu—Zn, Cu—Ni, Ag—Au); confirms that porosity formation is the rule rather than the exception. In general, one finds that the occurrence and distribution of porosity varies from system to system, and depends on the type of diffusion couple and on the concentration gradient present in the system. The smallest concentration difference between the two sides of the couple gives the smallest amount of porosity.

The porosity is usually formed near the Kirkendall interface on the side of the couple which contains the larger amount of the faster diffusing component. In most diffusion couples one finds that the region of porosity is fairly stationary and remains near the diffusion interface throughout the diffusion process. In silver—gold, however, several investigators have noted a movement of the region of maximum porosity away from the interface (17, 28, 32).

In vapor-solid couples, which have been extensively explored by Balluffi and co-workers (27, 32), a volatile metal is diffused out of or into an alloy through the vapor phase. In such couples it has always been found that porosity is formed when a volatile metal is removed from the alloy by evaporation. Similarly, a region of porosity is found when silver is diffused into gold, while none is observed when zinc is diffused into copper or copper into nickel. Balluffi *et al.* show that vapor-solid couples offer certain advantages

compared to sandwich-type couples, particularly for a quantitative study of the marker shifts. Unfortunately, the method is restricted to systems where a substantial difference exists between the volatility of the two components. Balluffi & Alexander (27) have carried out a quantitative study of the porosity resulting from diffusion in copper—α-brass couples. They find that 30 to 40 per cent of the zinc which "moves out" in the diffusion process gives rise to porosity in the sample. They stress that such a large amount of porosity, if ignored, may cause appreciable errors in the measured diffusion coefficients.

There has been some disagreement between the different groups of investigators regarding the dimensional changes associated with the diffusion process. Da Silva & Mehl (18) reported no significant dimensional change in the direction normal to the diffusion flux. This is confirmed in recent work by Balluffi & Seigle (32), while Seith & Kottmann (17) and, more recently, Heumann & Kottmann (28) find that there is a reduction of the specimen cross-section in the region of maximum porosity, and a slight increase of the cross-section on the other side of the diffusion interface.

It was noted by Barnes (26) that the diffusion zone in sandwich couples of copper—α-brass and copper—nickel appears to have an unusual structure, presumably caused by the local lattice strains associated with the diffusion process. Laue back-reflection photographs confirmed that the diffusion zone had developed a subgrain structure (polygonization). Similar observations have been made by Balluffi & Seigle (32) for vapor-solid couples of copper—α-brass and silver—gold.

Interpretation and theory of the Kirkendall effect.—It was pointed out by Seitz (33) that it was possible to interpret the Kirkendall effect by postulating a vacancy current balancing the difference in migration rates of the two diffusing elements. This idea was further developed by Bardeen (34), who showed that diffusion via vacant lattice sites leads to Darken's phenomenological relations, if it is assumed that the concentration of vacant lattice sites is everywhere in thermal equilibrium. Later on Seitz pointed out that the Kirkendall effect could equally well be interpreted in terms of an interstitial mechanism, and that Darken's relations would also follow in this case (35). He further stresses that the existence of this effect must rule out as a major contributing mechanism to the diffusion the process of direct interchange, and also generalizations of this mechanism such as the ring proposed by Zener [(36) see discussion of mechanism below].

A general phenomenological theory for vacancy diffusion was developed by Bardeen & Herring (13). They find that the relationship between radioactive and chemical diffusion coefficients given by Darken (equations VIII and X, above) will follow (*a*) if the vacancies are maintained in local equilibrium, and (*b*) if it is assumed that the cross-terms (equation III, above), which relate the flux of one constituent to the chemical potential gradient of another, are negligible. Neglect of the cross-term gives an error of the order of $1/z$, where z is the number of nearest neighbors surrounding a lattice site.

Bardeen and Herring also discuss the nature of the lattice processes which are necessary to maintain the concentration of lattice vacancies close to the equilibrium value. Sites which can act as sources and sinks for vacancies are at surfaces, at pores, at grain boundaries and particularly at dislocations. They point out that local plastic deformation may cause extensive vacancy production, e.g., through the action of Frank-Read (37) dislocation sources. The intimate relation between diffusion and dislocations seems to be confirmed by the afore-mentioned observations of Barnes (26) and of Balluffi & Seigle (32) on polygonization occurring in the diffusion zone. It may here be mentioned also that Buffington & Cohen (38) observed an increase in the rate of self-diffusion in α-iron when the specimen was subject to high temperature creep. The most straightforward interpretation of their results is to assume that the additional lattice defects which are formed by the plastic deformation enhance the diffusional effect due to the thermally-activated defects. The general problem of vacancy generation by means of moving dislocations has been reviewed by Seitz (39).

In the afore-mentioned discussions of the Kirkendall effect it was assumed that the vacancy concentration was at or near the equilibrium value. The more recent observations, which indicate a universal appearance of porosity whenever the Kirkendall effect is strong, have resulted in a reappraisal of this viewpoint. Seitz (39), in a detailed discussion of this problem, points out that the occurrence of pores must be related to the supersaturation of the lattice in some region with respect to vacancies. Small voids, cracks, and inclusions may act as nuclei for the production of larger pores. His calculations indicate that in typical cases vacancies will condense on spherical voids containing the volume equivalent of about 1000 vacant lattice sites if the supersaturation of vacancies is of the order of two or greater. In a perfect lattice, on the other hand, supersaturations of the order of 100 or more may be required. He also points out, however, that nuclei responsible for porosity may operate at very low supersaturations, perhaps of the order of 0.01.

Balluffi (40) presents further metallographic evidence in support of heterogeneous nucleation of the supersaturation of vacancies. From observation of the distribution of porosity in various sandwich-type diffusion couples he estimates that the relative excess concentrations required for precipitation of vacancies to form pores are of the order of 0.01 or less. Balluffi also suggests that the difference in porosity distribution for the same type of diffusion couple reported by different investigators may be due to variations in the concentrations of nuclei in the specimens used. This variation makes it difficult to compare in detail the results on porosity obtained at different laboratories.

The general formation of porosity in interdiffusion couples is of serious concern to the workers in the field, who, in general, still use the Boltzmann-Matano procedure in evaluating their data. This is so because this analysis assumes the conservation of lattice points and the maintenance of a con-

stant effective diffusion cross-section. In order to overcome this difficulty Seith & Kottmann (17) suggested a new method of analysis, based on application of Fick's 1st law alone. The method is further explored and discussed by Heumann (41) and by Heumann & Kottmann (28).

These investigators also consider the conditions necessary for formation of porosity in the lattice, and discuss the problems associated with diffusion couples where intermediate phases are formed. More recently a somewhat different formal treatment of the conditions required for porosity formation has been presented by Balluffi and Seigle (42).

Other work on substitutional chemical diffusion.—The use of the internal friction technique for the study of atom mobilities in solids has recently been reviewed in considerable detail by Nowick (43). The method has been particularly useful in the study of diffusion of interstitial solutes in b.c.c. metals (see below). However, it has also found some application in the study of substitutional diffusion, although the interpretation of the results in this case is less straightforward. The method was used by Nowick and co-workers in very extensive studies of diffusion in solid solutions of zinc in silver (8, 44, 45), and later by Ang & Wert (46) in a study of gold-nickel alloys; by Damask & Nowick (47) for a study of precipitation controlled by diffusion in aluminum-silver alloys; by Kunitomi (48) for a study of α-brass; and by Childs & Le Claire (49) in an investigation of copper-zinc, copper-aluminum, and platinum-nickel alloys. The latter authors also give a comparison between the results obtained by conventional diffusion methods and by the internal friction technique.

We have mentioned the apparent deviations from Arrhenius's law obtained by Nowick. Possible explanations of these results have been discussed in a paper by Crussard (50).

The Mechanism of Diffusion

Theories of H and D_o.—It is recalled that Huntington & Seitz (51, 52), as a result of detailed quantum mechanical calculations on self-diffusion in copper, concluded that the vacancy mechanism of diffusion is strongly favored on energetic grounds. The calculations indicated a heat of activation for vacancy diffusion of the order of 2.5 to 2.8 ev., while the corresponding figures for the interstitial and direct exchange mechanism were of the order of 10 ev or more. In a recent paper Huntington (53) revises the estimate for the interstitial mechanism, now giving a value of 4 to 5 ev. Practically all this energy is used for excitation of the atom to the interstitial position, while the heat of motion is found to be of the order of 0.25 ev. or less. The experimental value of H is about 2 ev., and the vacancy mechanism is still strongly favored.

Zener pointed out (36) that a simultaneous rotation of four atoms in a ring would involve a considerably lower heat of activation than either of the two mechanisms ruled out by Huntington & Seitz. Even so, the heat of

activation for self-diffusion in copper calculated by Zener for the ring mechanism was still higher than that for a vacancy mechanism. However, Zener argued that the ring mechanism would be relatively easier in a b.c.c. lattice, and might there compete seriously with the vacancy mechanism.

Paneth (54) showed that in a b.c.c. metal such as sodium, interstitial defects of a heretofore unconsidered kind, so-called "crowd-ions," might also, from an energetic point of view, compete with the other mechanisms.

While the experimental values of H for diffusion in metals generally fall between 10 and 100 kcal./mole, the reported data on D_o for chemical diffusion range from 10^{-9} to 10 cm.^{2}/sec. For self-diffusion D_o appears to fall in the more restricted range 0.1 to 10. There have been a number of theoretical and semiempirical studies aiming at an understanding of these surprising facts. Work up to 1949 was very adequately reviewed by Le Claire (2).

Recent theoretical work on D_o has, in large measure, been based on the pioneering research of Wert & Zener (55, 56), prompted by Wert's experimental determination of D_o and H for the diffusion of interstitial solutes in b.c.c. iron. The theory was originally restricted to this type of diffusion only, but was later extended by Zener (57, 58) to cover also self-diffusion and low-concentration chemical diffusion in substitutional solid solutions.

Wert & Zener assume that the problem of diffusion may be considered one of three-dimensional random walk, and derive the following expression for the diffusion coefficient in a cubic metal.

$$D = \gamma a^2 \nu \exp(-\Delta G/RT)$$

Here γ is a numerical factor of the order of unity which is uniquely determined by the lattice geometry and the assumed diffusion mechanism; a is the lattice parameter, while ν is the frequency of vibration of the diffusing element in an equilibrium position. ΔG is defined as the reversible, isothermal work required in moving an atom through an equilibrium psoition to the saddle-point configuration. If we make the usual separation of ΔG into the appropriate heat and entropy terms, we may write

$$D = D_o \exp(-H/RT) = \gamma a^2 \nu \exp(\Delta S/RT) \exp(-\Delta H/RT)$$

We identify ΔH with the heat of activation, while, similarly, ΔS defines an entropy of activation. If diffusion proceeds by thermally activated lattice imperfections, we may consider the thermodynamic quantities to be the sum of two terms, one due to the formation of the imperfection (i.e., the vacancy) and the other term due to its motion. Among the quantities appearing in the expression for D_o, only ΔS is associated with a considerable uncertainty. Wert & Zener estimate ΔS by making use of the elementary thermodynamic relation between ΔS and ΔG. They point out that ΔG according to their definition should decrease with increasing temperature due to the general loosening of the lattice. Therefore, a positive entropy of activation is always anticipated. They suggest that the major part of ΔG presumably is expended in

straining the lattice, and arrive at a numerical estimate of ΔS by assuming that the temperature coefficient of ΔG will not differ greatly from the corresponding temperature coefficient of the shear or tensile modulus. For the diffusion of small solute atoms (e.g., C, N, O) on the interstitial sites of a b.c.c. metal like α-iron, they find reasonable agreement between theory and experiment by assuming that all the activation energy goes into lattice straining. More recently, Ang (59) has found similar agreement in a number of other b.c.c. systems. For vacancy diffusion, Zener (*loc. cit.*) argues that the entropy of vacancy formation and the entropy of motion should both be positive, although in this case only a fraction of the activation energy goes into lattice strain. From the available data on self-diffusion and tracer diffusion in essentially pure metals Zener finds agreement with his theoretical expression with a fraction of 0.55.

However, the great bulk of chemical diffusion data accumulated from about 1930 and on seemed to indicate that for chemical diffusion H was much lower than for self-diffusion, and also that large negative entropies of activation were quite common. Zener suggests that these data did not result from a genuine lattice diffusion process, and that the data might be seriously in error due to the presence of structural short-circuiting paths such as grain boundaries, etc.

This viewpoint is adopted by Nowick (60), who critically reviews and reinterprets the available information on chemical diffusion in dilute solid solutions. Accepting only the diffusion data for high temperatures as representing true lattice diffusion, and making use of Zener's theory for D_o he calculates new values for H for a number of alloy systems. In a recent paper Tomizuka & Slifkin (61) compare Nowick's values of D_o and H with their more recent experimental values for diffusion of radioactive tracers of cadmium, indium, tin, and antimony in single crystals of silver. The agreement is remarkably good.

Since Zener's theory first appeared there have been several attempts to extend the treatment by the introduction of various refinements. Dienes (62) points out that Fensham's data on the self-diffusion in single crystals of tin (63) lead to a negative entropy of activation, although the existence of short-circuiting paths presumably can be ruled out in this case. He suggests [see also Vineyard & Dienes (64)] that for a vacancy mechanism the total entropy of activation may be considered a sum of two terms: (*a*) A positive term, ΔS_a, results from the reduced vibrational frequency surrounding a lattice vacancy. Following Mott & Gurney (65) he sets $\Delta S_a = zR \ln \nu/\nu'$, where ν is the vibrational frequency of the unperturbed atoms, ν' is the frequency of atoms neighboring on a vacant lattice site, while z is the number of nearest neighbors. (*b*) A negative term, ΔS_b, is due to the increased vibrational frequency around the saddle point configuration. Dienes argues that ΔS_b may sometimes outweigh ΔS_a, and give rise to a net negative entropy of activation.

Huntington, Shirn & Wajda (66) conclude from similar arguments that

for certain types of lattice defects in f.c.c. metals a negative activation entropy may be expected.

Le Claire (67) and later Buffington & Cohen (68) have suggested other extensions of Zener's theory. Their work in general attempts to relate the experimental values of D_o and H for self-diffusion in f.c.c. and b.c.c. metals to other measurable physical quantities such as cohesive energies, lattice constants, expansion coefficients, and elastic constants. From such correlations Le Claire attempts to make a choice among the various possible diffusion mechanisms. He concludes that the experimentally observed values of D_o and H for self-diffusion are consistent only with a vacancy mechanism in f.c.c. and a ring mechanism in b.c.c. metals. The afore-mentioned recent information on the Kirkendall shift in certain b.c.c. alloys (23, 24) seems to indicate that these conclusions are probably incorrect.

Buffington & Cohen consider the vacancy mechanism only, and propose, among other things, a procedure for evaluating the fraction (λ) of the activation energy which goes into lattice straining in the elementary diffusion act. Based on experimental data for lead, copper, silver, and gold they give for f.c.c. metals $\lambda = 0.64$, which is in reasonable agreement with Zener's empirical value of 0.55. For b.c.c. metals the data are inadequate, but a tentative value of λ is 0.84.

Buffington & Cohen also point out that the recent data on self-diffusion in b.c.c. sodium (91), not considered by Le Claire, do not rule out a vacancy mechanism for this metal even by Le Claire's own criteria.

Separation of heat of formation and heat of motion for lattice imperfections.—There have been two recent theoretical estimates of the heat of formation of lattice vacancies. Kochendörfer (69) considers a vacancy as equivalent to a section of two dislocations of opposite sign located at neighboring glide planes. From this model he calculates the heat of formation of single vacancies to be 1.2 ev. in copper, 1.1 ev. in silver and gold and 1.75 ev. in α-iron. Fumi (70) considers the vacancy as an impurity of zero valency, and obtains somewhat higher values, e.g., 1.9 ev. for copper, 1.4_5 ev. for silver, and 1.5 ev. for gold.

It is conceivable that vacancy diffusion in solids actually proceeds by means of associated vacancies, the simplest case being the vacancy pair consisting of two vacancies located on neighboring lattice sites. Theoretical work by Bartlett & Dienes (71) indicates that the heat of activation for the motion of a double vacancy in any face-centered cubic metal should be about one half of that for a single vacancy. They also estimate the energy of dissociation for a vacancy pair in copper to be of the order of 0.6 ev. If we assume a value of 1.5 ev. for the formation of a single vacancy in copper, we find that the mole fractions of single and double vacancies at the melting point should be of the order of 10^{-4} and 10^{-6}, respectively.

In recent years, much attention has been given to the design of experiments which permit separate determinations of the heat of formation and the heat of motion of lattice imperfections. In such investigations conventional

diffusion methods are generally of little use, although Berkowitz, Jaumot & Nix (72) may have achieved such a separation in studies of diffusion in a nickel-aluminum alloy.

Nowick & Sladek (44), in their study of diffusion in silver-zinc alloys by means of the internal friction method, may also have achieved a separation of the total heat of activation into the appropriate formation and motion terms. They quenched alloy specimens from 300–400°C., and observed the variation of the initial relaxation time with the temperature of the measurements. For an alloy containing about 30 atom per cent zinc Nowick finds 12 to 14 kcal./mole (0.5 to 0.6 ev.) for the heat of formation and 17 to 20 kcal. (0.75 to 0.85 ev.) for the heat of motion.

Carpenter (73) interprets the excess heat capacity found in certain metals as arising from the formation of lattice imperfections. From heat capacity data he deduces a value of 6 kcal./mole for the heat of formation of these imperfections in sodium and potassium.

There have been several attempts to evaluate the concentration of lattice imperfections (presumably vacancies) from precise determination of changes in electrical resistance. Experiments designed to achieve this under equilibrium conditions have been reported by MacDonald (74) for lithium, sodium, and potassium, and by Meechan & Eggleston (75) for copper and gold. In both investigations the concentration of imperfections is assumed proportional to an "excess electrical resistance." However, in these cases there is some doubt whether the observed excess electrical resistance is due only to the postulated lattice imperfections.

In this respect, the work by Kauffman & Koehler (76) seems less ambiguous. These investigators quenched high purity gold wires from given temperatures in the range 500–900°C. to liquid nitrogen temperature. The resistance of the wire was then compared with that of an identical specimen which had not been heated, and increases in electrical resistance of up to 9.8 per cent were found. The resistance increase is interpreted as due to lattice vacancies that are in equilibrium at the temperature at which the quench is made. The slope of the logarithm of the resistance increase versus the reciprocal of the absolute temperature at quench gives 1.28 ± 0.03 ev. for the heat of formation of a vacancy. The wire is then subjected to a recovery anneal near room temperatures. The recovery is assumed to be due to the precipitation of the excess concentration of vacancies at dislocations, grain boundaries, sub-boundaries, etc. If this interpretation is correct, the heat of activation of the recovery process, 0.68 ev. may be identified with the heat of activation for motion of vacancies through the lattice. The sum of the two heats of activation, 1.96 ev., is in excellent agreement with the most recent determination of the heat of activation for self-diffusion in gold [Gatos & Kurtz (77)]. However, the older determinations give somewhat higher values.

Dexter (78) and Jongenburger (79) have given theoretical estimates of the effect of lattice vacancies on the electrical resistivity of f.c.c. metals. If

their estimates are used, one finds from the data of Kauffman & Koehler that pure gold contains a mole fraction of vacancies of the order of 10^{-4} at the melting point. This is in good agreement with the value derived from thermodynamic principles alone.

The recovery of metals from the bombardment with high-energy particles and from cold work has been studied by a number of investigators. The observations have been interpreted in terms of the motion and annihilation of lattice imperfections formed as a result of the previous treatment. Experimentally, the recovery process has usually been indicated by the accompanying change in electrical resistivity. A recent review of this work has been given by Broom (80), and we shall here only give an outline of the results.

The increased electrical resistance resulting from the bombardment with electrons and nucleons is in part annealed out at temperatures below room temperature, and there is evidence for two different thermally activated processes of recovery. In copper, silver, and gold the observed heats of activation are 0.2 to 0.3 ev. for the process occurring at the lowest temperatures (around −150°C.), and 0.6 to 0.8 ev. for a process taking place about 50° below room temperature. Similar results with very nearly the same heats of activation have been reported by Manintveld (81) for the recovery of low-temperature cold work in these metals. It is now commonly assumed that the recovery process occurring at the higher temperatures is due to the migration of lattice vacancies, while the process which takes place at the lower temperatures has offered a fertile field for speculation. The process may be due to interstitial migration, to migration of vacancy pairs, or to the recombination of closely spaced vacancy-interstitial pairs. As a result of work both on the recovery of electrical resistance and on the release of stored energy resulting from the irradiation of copper, Overhauser (82, 83) argues that the recovery occurring around −15°C. in this metal may be due to a recombination of vacancies and interstitials through interstitial diffusion.

There is at the present time an urgent need for methods of measurement which allow a distinction to be made between the different types of imperfections introduced by irradiation or by cold work. The recent work by Tucker & Sampson (84) is a step in this direction. They suggest that precision determinations of lattice parameters may permit identification of the imperfection as being predominantly vacancy or predominantly interstitial. Such information may also possibly be obtained from a study of the small volume changes associated with the production or annealing of imperfections [McDonell & Kierstead (85)].

There has been an effort by several investigators to secure information on the nature of lattice imperfections from the study of atom movements in ordering alloys. In alloys such as Cu_3Au the kinetics of the ordering process in specimens quenched or irradiated, or both, has been explored recently from this viewpoint by Brinkman, Dixon & Meechan (86), by Blewitt & Coltman (87), and by Dugdale & Green (88).

Self-Diffusion and Solute Diffusion

Self-diffusion in pure metals and alloys.—Data on the rate of self-diffusion in lithium were reported by Gutowsky & McGarvey (5), and similar information for sodium is available through the work of Gutowsky (89), Norberg & Slichter (90) and Nachtrieb and co-workers (91, 92). In the three first mentioned investigations the new nuclear resonance technique was adopted, and the results for sodium agree well with those obtained in Nachtrieb's tracer studies.

Nachtrieb *et al.* also investigated the effect of hydrostatic pressure on the rate of self-diffusion in sodium. At 1 atm. pressure they found the heat of activation to be 10.45 kcal./mole, while at 8000 atm. the figure is 12.06 kcal. The corresponding change in D_o is from 0.242 to 0.176 cm.²/sec. They also note an interesting correlation between the experimental heat of activation and the melting point of sodium, both considered as functions of pressure.

$$H(P) = 14.2\ RT_m(P)$$

This expression is formally analogous to various expressions proposed earlier in order to correlate self-diffusion in different cubic metals with their melting points. The most successful of these expressions appears to have been the one suggested by van Liempt (93):

$$H = 32\ T_m.$$

Previously, there had also been an attempt to correlate H with the heats of evaporation. Nachtrieb *et al.* propose a new semiempirical relation $H = 16.5\ L$ where L is the molar heat of fusion. This expression holds strictly for sodium at 1 atm. pressure, and they show that it is satisfied to within a few per cent for a large number of cubic metals. So far, the only significant discrepancy is found for lead where the calculated value of H is 25 to 30 per cent below the experimental value. A recent redetermination of the heat of activation for self-diffusion in lead shows that this discrepancy is indeed a real one [Okkerse (94)]. This correlation led Nachtrieb & Handler (95) to the idea that the lattice imperfection responsible for diffusion is also responsible for the process of fusion. They propose that the relaxed vacancies present in the liquid state may have their analogue in the solid state, and that diffusion in solids involves small liquid-like regions in the lattice consisting essentially of a vacancy and its nearest neighbors.

If ΔG is the free energy of activation for diffusion, we may, from elementary thermodynamics, derive an expression for the so-called activation volume $\Delta V = (\partial \Delta G/\partial P)_T$. This volume has a significance analogous to that of the other activation quantities; i.e., ΔV is the molar change in volume associated with the elementary diffusion act. When diffusion is studied as a function of pressure, the activation volume may be determined experimentally. For self-diffusion in sodium Nachtrieb *et al.* obtain an activation volume of 12.3 cc./mole at 1 atm., while the corresponding value at 8,000 atm. is 8 cc. The activation volume is roughly one half of the gram atomic volume. The

sign and magnitude of ΔV is considered by Nachtrieb and co-workers as evidence in favor of a diffusion mechanism by relaxed vacancies.

Liu & Drickamer (96) have reported a series of measurements on self-diffusion in zinc, both parallel and perpendicular to the hexagonal axis. They carried out their measurements both under hydrostatic pressure and under compressive stresses parallel and perpendicular to the diffusion direction. In all cases it was found that the rate of self-diffusion was reduced by the application of the compressive stress. Very recently, Lawson (97) has pointed out that Liu & Drickamer's data show internal inconsistencies which suggest the presence of some systematic error in the measurements.

The anisotropy of self-diffusion in zinc at atmospheric pressure has also been studied by Shirn, Wajda & Huntington (98). The results differ somewhat from the data reported by Liu & Drickamer and from the older data of Miller & Banks (99). From their results on diffusion anisotropy Shirn *et al.* conclude that in this metal two mechanisms are active in the diffusion process. They believe that at least one of these, and possibly both, are vacancy mechanisms.

In the past couple of years there have been new investigations of the self-diffusion in polycrystalline tantalum by Eager & Langmuir (100) and in polycrystalline magnesium by Shewmon & Rhines (101). The experiments on tantalum had to be carried out at extremely high temperatures (1800–2500°C.) in order to overcome the difficulties associated with the rapid rate of grain-boundary diffusion.

The rate of self-diffusion in gold has been redetermined by Gatos & Kurtz (77). They used a new autoradiographic method, and their results differ somewhat from the older data reported for this metal.

Johnson & Martin (102) have explored the effect of previous intense proton bombardment on the rate of self-diffusion in silver, but find no measurable effect.

In certain cases the rate of self-diffusion in pure metals appears to be quite sensitive to the presence of relatively small amounts of impurities. Thus, Hoffman & Turnbull (103) noted that small quantities of dissolved lead increased the rate of self-diffusion in silver. Okkerse (94), on the other hand, has recently found that about 1 per cent of silver, cadmium, or tin has little or no effect on the rate of self-diffusion in lead. For silver in lead this is in agreement with earlier observations by Seith & Keil (104).

Sonder (105) has studied the rate of diffusion of silver and antimony tracers in single crystals of silver and found results in general agreement with those of Hoffman & Turnbull. Thus, he notes an increase of about 50 per cent in the rate of self-diffusion of silver in an alloy containing 0.8 per cent antimony. However, as no change in the heat of activation is observed for alloys containing up to 1.6 per cent antimony, the effect is presumably particularly noticeable in the preexponential term, D_o. The effect of impurities on the rate of diffusion has been discussed from a theoretical point of view by Overhauser (106) and by Lazarus (107).

Kuper & Tomizuka (108) have determined the rate of diffusion of radioactive tracers of both copper and zinc in ordered and disordered β-brass containing 48 per cent zinc. The results indicate that in the disordered range the mobility of the zinc atoms is roughly twice the mobility of the copper atoms. Below the order-disorder point the diffusion rates of both components are substantially reduced, and it is found that the two intrinsic diffusivities approach each other as the temperature is lowered. This is considered as support for a vacancy rather than an interstitial mechanism.

Diffusion of impurities in pure metals.—The results of Slifkin and coworkers (7, 61) on the rate of diffusion of small amounts of radioactive tracers of cadmium, indium, tin, and antimony in pure silver have been mentioned. Martin, Johnson & Asaro (109) reported similar work on the diffusion of gold in copper.

In all these cases there is only a small difference between the observed rate of self-diffusion of the pure solvent metal and the rate of diffusion of the impurity solute. In the silver to antimony series there is, however, a clear trend towards lower values of both H and D_o as we increase the atomic number of the solute. These results seem to indicate that recent speculations by Le Claire (67), that the difference between solute diffusion and solvent diffusion would vanish at sufficiently small concentrations, are unfounded. Similarly the data give no support for the idea, apparently first advanced by Johnson (110), that there may be a particularly strong binding between the solute atom and a vacancy located at a neighboring lattice site. This idea represented an attempt to account for the high diffusion rates believed to exist in low concentration chemical diffusion.

Prompted by the experimental results obtained by Slifkin *et al.*, Lazarus (111) has developed an atomistic theory which in large measure accounts for the trend observed in their results. The basic assumption on which this work is based is that the solute atoms, i.e., cadmium, indium, etc., differ from the solvent atoms only in the nuclear charge and in the number of valence electrons inserted into the lattice in place of the solvent atom. The principal objective of the theory is to calculate the differences between the values of H and D_o for self-diffusion and for low concentration solute diffusion.

The change in the heat of formation of a lattice imperfection in a nearest-neighbor position to the solute atom is calculated from an estimate of the change in coulomb energy, assuming a screened coulomb potential.

The change in the heat of motion is assumed to result entirely from the change in the elastic shear strain energy associated with the jump of the diffusing atom into the imperfection site. Lazarus here calculates the effect of the changed coulomb energy on the appropriate elastic constants.

Using the screening constant q, derived by Mott (112) from the Thomas-Fermi approximation, Lazarus finds remarkably good agreement between calculated and observed values of H and D_o for antimony in silver. However, if the screening constant is assumed to be the same for different solute elements, the method does not give equally good agreement for the other solutes in silver [Tomizuka & Slifkin (61)].

It is a consequence of Lazarus's theory that solute atoms with a "metallic valence" lower than the solvent, i.e., for silver the transition elements ruthenium, rhodium, and palladium which precede silver in the periodic system, should show higher values of D_o and H than the solvent. Still unpublished results on the diffusion of radioactive tracers of ruthenium in silver seem to confirm this prediction (61).

Diffusion of nonmetallic solutes in metals.—Since the early internal friction studies of Zener and co-workers (*loc. cit.*) on the diffusion of nonmetallic solutes in metals, there have been a number of similar investigations where these techniques were adopted. The rate of diffusion of carbon and nitrogen in α-iron has recently been redetermined by Thomas & Leak (113), and the diffusion of nitrogen by Fast & Verrijp (114). The rate of diffusion of oxygen and nitrogen in tantalum and niobium have been studied by Ang (59), who used a low-frequency technique and by Marx, Baker & Sivertsen (9) who used higher frequencies. Although the latter authors find a dependence of H on temperature, the results of the two investigations are in good agreement in the temperature range where they overlap.

Wert (115) has explored the effect of small amounts of nickel, molybdenum, chromium, manganese, and vanadium on the rate of diffusion of carbon in α-iron. He finds that the presence of these elements in amounts of about one half per cent does not sensibly affect the diffusion rate.

Adopting chemical diffusion methods, Busby, Warga & Wells (116, 117) have studied diffusion of boron in iron and steel, Demarez, Hock & Meunier (118) have investigated the diffusion of hydrogen in steel, Lander, Kern & Beach (119) have explored the diffusion of carbon in nickel, while Mallett and co-workers (120) have studied the diffusion of nitrogen in β-zirconium.

Smith (121) has measured the diffusion of carbon in iron by a steady-state method, i.e., a method based on the direct application of Fick's 1st law.

Grain-boundary and surface diffusion.—It has long been known that grain boundaries as well as external and internal surfaces offer less resistance to diffusion of substitutional atoms than does the lattice of a single crystal. Under certain conditions the grain boundaries and surfaces may act as effective diffusion short-circuiting paths, thus giving rise to erratic results in diffusion experiments designed to give information on lattice diffusion alone (10). In fact, many of the sometimes puzzling results obtained in older chemical diffusion experiments are now attributed to the existence of these paths of easy diffusion (57, 60).

It is now generally recognized that small-angle grain boundaries may be described quite well in terms of a dislocation model proposed by Burgers (122). Let us consider the small-angle boundary formed by fitting together two cubic crystals misoriented by an angle θ around a common [100] axis. According to the Burgers' model this boundary will consist of an array of parallel dislocation lines or "pipes." If the lattice spacing is a, the distance between neighboring dislocation lines will be [Read & Shockley (123)].

$$d = a/(2 \sin \theta/2)$$

However, this simple model breaks down when the angle θ becomes so large

that the distance d is of the order of the lattice spacing or less. Further complications are introduced if the [100] axes deviate from parallel alignment by an angle ϕ.

The careful work by Hoffman & Turnbull (10) on grain boundary self-diffusion in silver showed that the grain boundaries formed by the randomly oriented crystals in a polycrystalline specimen are indeed very effective short-circuiting paths for the diffusion process. Adopting Fisher's method of analysis (124), and taking the value 5.10^{-8} cm. for the thickness of the grain boundaries, they report the following expression for the dependence of the grain boundary diffusion coefficient on temperature in high purity silver

$$D_{\phi} = 0.03 \exp(-20.200/RT) \text{cm.}^2/\text{sec.}$$

For lattice diffusion they give

$$D = 0.895 \exp(-49.500/RT) \text{ cm.}^2/\text{sec.}$$

Okkerse (94) has recently reported equivalent data for grain boundary diffusion in polycrystalline lead, and Wajda (125) for zinc. For simultaneous grain boundary and lattice diffusion these studies show that grain boundary migration is making the most significant contribution to the "effective diffusion coefficient" at the lower temperatures. At very high temperatures the lattice diffusion proper usually takes over.

Smoluchowski and co-workers (126, 127) studied the diffusion of silver and zinc into columnar copper grains approximately aligned along a common [100] axis. Their technique consisted of removing successive layers from the diffusion sample, and etching the surface with reagents which defined a certain concentration of the diffusing metal. They explored the penetration as a function of angular misorientation of the grains, and found a maximum penetration around $\theta = 45°$. However, they were unable to detect any preferential grain boundary diffusion for low angle boundaries, $\theta < 10°$ for silver into copper and $\theta < 18°$ for zinc into copper. From these studies they concluded that a small-angle boundary which, according to the dislocation model, consists of isolated dislocation "pipes," does not facilitate diffusion in the direction of the pipe. Smoluchowski goes on to develop a semiquantitative theory which relates the grain boundary diffusion coefficient to this angle of misfit (128). Later on, Haynes & Smoluchowski (129) have studied the grain boundary self-diffusion in bicrystals of b.c.c. iron oriented along a common [110] direction. Measuring the angle of misfit between crystallographic axes in the [110] plane, they once more find little or no penetration for angles below a certain value (20°), and increasing penetrations along the grain boundaries up to the maximum angle of misfit studied (85°).

Couling & Smoluchowski (130) have studied the anisotropy of grain boundary diffusion at angles $\phi = 0°$, 45°, and 90° in bicrystals of copper. They report that anisotropy is significant at 0° and 90°, but small or nonexistent at $\sim$45°.

The results reported by Smoluchowski *et al.* seem to be contradicted by recent results obtained by Turnbull & Hoffman (131). These investigators

study the rate of self-diffusion in grain boundaries formed by bicrystals of silver, misoriented by a rotation θ around a common [100] axis. They explore the range $9° \leqq \theta \leqq 28°$, and find that within experimental uncertainty the measured grain boundary diffusion coefficients are independent of θ. In evaluating their results they make the usual assumption that $D_{gb} \gg D_l$. For the dependence of D_{gb} on T they give

$$D_{gb} = 0.14 \exp(-19.700/RT) \text{ cm.}^2/\text{sec.}$$

The observed heat of activation is in good agreement with the value found by the same authors for diffusion in grain boundaries formed by randomly oriented crystals. In terms of the afore-mentioned dislocation model the results indicate that even fairly widely separated dislocation pipes are effective in accelerating the diffusion process.

Using a differential method of measurement Hendrickson & Machlin (132) have recently studied the rate of self-diffusion of silver along polygonized small-angle boundaries in silver. Their results, which are restricted to one temperature only, are in reasonable agreement with the data of Hoffman & Turnbull, and appear to contradict Smoluchowski and co-workers.

It is generally supposed that the rate of surface diffusion is very much faster than grain boundary or lattice diffusion, both for self-diffusion and for diffusion of a foreign atom on a different substrate. There is much qualitative evidence in favor of this view, but only few quantitative measurements. Nickerson & Parker (133) reported quantitative data for the rate of surface self-diffusion of radioactive silver on silver. The observed activation energy was approximately half of that given by Hoffman & Turnbull for grain boundary diffusion. Menzel (134) has studied surface self-diffusion on single crystals of copper, and reports a strong influence of the atmosphere. Winegard & Chalmers (135) studied self-diffusion at silver surfaces, and Winegard (136) has later found that surface self-diffusion on single crystals of silver is isotropic on the [100] and [111] planes, but depends on direction on the [110] plane, the diffusion being faster in the [110] than in the [100] directions. The difference in surface-diffusion rates at different crystal faces has been explored both theoretically and experimentally by Drechsler (137). In the diffusion of barium on tungsten surfaces he finds activation energies ranging from 0.20 to 0.76 ev. (!). In this work Drechsler uses the field emission technique, first adopted by Müller (138) in a study of the surface self-diffusion of tungsten. The same technique has also been applied by Gomer & Hulm (139) in a study of the mobility of oxygen on the surface of tungsten and by Klein (140) for carbon on tungsten. Gomer (141) has used this technique for a rough evaluation of the heat of activation for the diffusion of silicon in bulk nickel.

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RADIATION CHEMISTRY AND HOT ATOM CHEMISTRY[1]

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Introduction

Radiation chemistry deals with the chemical effects of high-energy radiations such as x-rays, γ-rays, α-particles, β-particles and charged particles raised to high energy by accelerating machines. In passing through matter all of these radiations lose their energy by transferring it to electrons, thus producing electronically excited or ionized molecules. Chemical effects follow as a result of the transfer of the energy of electronic excitation or ion neutralization into vibrational energy sufficient to break bonds. Most of these chemical events result in the formation of free radicals which may combine with each other or react with other species of the medium, their fate being determined by their proximity to each other and the activation energies of possible competing reactions.

Radiation chemistry is different from photochemistry (activation of chemical reactions by visible and ultraviolet light) in important respects. Whereas in photochemistry it is possible to activate reactions with monochromatic light which produces a single well-defined excited state, in radiation chemistry the high-energy charged particles are not selective; they may produce many different excited states and different ions. Another difference is that in photochemistry each photon excites only one molecule and the excited molecules are distributed homogeneously throughout the system, whereas in radiation chemistry the energy of each incident photon or particle is sufficient to produce many ionized and many excited molecules. These are concentrated along the path of the high-energy particle in such a way that in liquid or solid systems the radicals produced have a much higher probability of reacting with neighbors in the same track than with similar species from other tracks. Heavy, relatively slow moving radiations such as α-particles produce tracks of essentially continuous ionization and excitation, while high speed electrons knock out secondary electrons only every thousand angstroms or so along their paths. The secondary electrons usually have sufficient energy to ionize several molecules in close proximity to the parent ion and so form "spurs" or "hot spots" of reactive fragments which may combine with each other, or, if they escape this fate, have a chance of encountering fragments from an adjacent spur. Ionization density in the tracks, diffusion, and caging effects thus may play a major role in determining the types and yields of stable products formed.

[1] The survey of the literature pertaining to this review was concluded in January, 1955.

[2] The writing of this chapter was done as part of work related to a research program supported by the Research Committee of the University of Wisconsin and by the United States Atomic Energy Commission.

Closely related to the field of radiation chemistry is the study of chemical effects of nuclear transformations. Processes such as the capture or emission of a high-energy particle or photon by a nucleus may cause the nucleus to recoil with high kinetic energy. Isomeric transition accompanied by emission of conversion electrons and auger electrons may produce an atom with high positive charge. In losing the high energy or charge the atom ruptures many bonds in its immediate vicinity. The result is a pocket of radicals similar to the "spurs" occurring in β-ray tracks. If, as is often the case, the atom is made radioactive ("tagged") by the nuclear process, there are methods for determining whether it enters stable chemical combination immediately after thermalization or not until it has undergone some diffusion in thermal equilibrium with the medium.

Because reactive atoms produced by nuclear transformations are born with energy greatly in excess of the average energy of atoms around them they are termed "hot" atoms and the study of their reactions is sometimes called "hot atom chemistry." The nucleus does not, however, hold exclusive rights to the production of hot atoms, they can also be produced by ultraviolet or visible light, by high-energy radiation, and by electrical discharges. In this chapter "hot atom chemistry" will be considered to mean the study of reactions of hot atoms and hot radicals, regardless of their ancestry, since such an interpretation allows a profitable correlation of results from somewhat different fields.

In the pages to follow some of the most recent work in the fields of radiation chemistry and hot atom chemistry will be summarized. Greatest emphasis will be placed on those investigations which seem, at the moment, to contribute most to an understanding of reaction mechanisms, or which contribute unique experimental information. In those areas which have recently been covered by reviews in this series only the literature of the last year will be cited, in others a longer range perspective will be presented.

For those relatively new to this field, introductory discussions of the physical mechanisms of absorption of high-energy radiation may be found in many books; two examples are those by Glasstone (1) and by Halliday (2). A comprehensive treatment of the subject has recently been given by Fano (3). Excellent discussions of radiation absorption with specific emphasis on mechanisms of importance in radiation chemistry are given by Platzman (4, 5), and by Franck & Platzman (6). Reviews of the literature of radiation chemistry are given by Burton (7), Dainton & Collinson (8), Allen (9), Weiss (10), and Hart (11) in preceding volumes of *Annual Review of Physical Chemistry*, and by Magee (12). Surveys of the fields of chemical effects of nuclear transformations [Willard, (13); Nesmeyanov, Sazonov & Sazonova, (14)], and of hot radical reactions [Hamill *et al.* (15)] are also available with references to the earlier literature.

"Hot" Reactions

Introduction.—A "hot" atom or "hot" radical is one which has been born

with energy much in excess of the average energy of the surrounding molecules and has not yet reached thermal equilibrium with them. If it reacts chemically before becoming thermalized the reaction is a "hot" reaction. Experimental criteria of such reactions are that they are temperature independent, are relatively insensitive to added reagents which would inhibit analogous thermal radical reactions, and, in the gas phase, are inhibited by the presence of inert gas which can thermalize the hot particle before it encounters a reactant molecule. Such reactions have been observed for radicals produced by nuclear transformation, in the gas, liquid and solid phases, for radicals produced by γ-rays in liquid and solid phases, and for radicals produced by ultraviolet light in gas and liquid phases. In a number of cases the reaction products are the same as those which one would expect from thermal radical reactions at elevated temperatures; in other cases, where the atom or radical energy is much higher than achieved in thermal processes a completely different product is obtained.

There are several interesting differences between hot radical reactions and thermal radical reactions from a theoretical point of view. One of these arises from the fact that a hot radical remains hot for only a limited number of collisions and must react in one of these if it is to react at all as a hot radical. For this reason the yield of such reactions, per radical formed, is low unless the "steric factor" is high. A typical hot radical can carry its excess kinetic energy through only a dozen or so collisions.[3] If the energy is vibrational it may survive a few thousand collisions (16, 17, 18). Whether or not the steric factor varies with energy so that a hot radical has greater probability of reacting at one stage in its life history than at another, has been a subject of speculation by several investigators (18 to 21). There is experimental evidence to indicate that such variation does occur in the case of hot hydrogen atoms (19) reacting with HI and I_2; and hot methyl radicals formed from CH_3I by 1849 Å light abstract hydrogen from CH_3I with higher yield than those formed by 2537 Å light (18). In the later case, there is some evidence, however, that the excess energy with 1849 Å light is vibrational.

A radical with high kinetic energy may be precluded by conservation of momentum requirements from taking part in a reaction which requires relatively low energy (19, 22). For example, if a high-energy iodine atom strikes a methane molecule a maximum of about 10 per cent ($M_{CH_4}/M_{CH_4}+M_I$) of its energy can go into internal energy of the activated complex ICH_4. Thus, if the reaction $I+CH_4 \rightarrow CH_3I+H$, which is about 50 kcal./mole endothermic, were to occur by a hot atom mechanism, dependent on kinetic energy of the I, the latter would have to be greater than 500 kcal./mole. The CH_3I formed would have over 450 kcal./mole of kinetic energy and in all probability would not survive its next collision.

Photochemical hot atom and radical reactions in the gas phase.—Although it follows directly from the law of conservation of energy that hot atoms and

[3] The average fraction of the energy lost per collision is $\Delta E/E = 2M_AM_B/(M_A+M_B)^2$, where M_A and M_B are the masses of the colliding particles.

radicals are produced in many photochemical dissociations, only a few examples of reactions attributed to them have been reported. This is probably due to the fact that the quantum yield of hot reactions is usually low, thus requiring a very high light intensity to produce observable effects during the time of a normal experiment. Most photochemical reactions have been studied under conditions where the rate of thermal reaction of the radicals is sufficient to mask the rate of a hot reaction.

The first investigators to interpret photochemical results in terms of hot radicals seem to be Ogg & Williams (23) who observed that the inhibiting effect of I_2 on the photolysis of HI is greater with an inert gas present than for pure HI, and ascribed this to the effect of the additive in moderating the hot (42 kcal./mole) H atoms produced by the 2537 Å light absorbed by HI. Schwarz, Williams & Hamill (19) showed that other inert gases increase the inhibiting effect of I_2 and that the relative effectiveness of these gases is such as might be expected if they act as moderators. Without added inert gas the photolysis is not influenced by the temperature, since all of the hydrogen atoms react while hot. With a high ratio of inert gas all reaction occurs after the atoms are thermalized, and the temperature dependence yields a value for the difference in activation energies between the reactions $H+HI \rightarrow H_2+I$ and $H+I_2 \rightarrow HI+I$. The ratio of steric factors for these reactions varies with the energy of the H atom.

In related work Carter, Hamill & Williams (24) have shown that, in mixtures of C_2H_6 and DI, hot deuterium atoms formed by the photolysis of DI react with C_2H_6 to form HD as well as with DI to form D_2. The ratio of these two products is a linear function of ethane concentration and independent of temperature up to a mole fraction of 0.7. At higher ethane pressures a temperature coefficient of the HD/D_2 ratio appears. The yield of HD is decreased by addition of He.

All work on photochemically produced hot radicals seems to have dealt with either H atoms from HI (discussed above) or with CH_3 radicals produced from CH_3I or $Hg(CH_3)_2$. Schultz & Taylor (25) using 2537 Å light to produce CH_3 radicals with 32 kcal./mole, from CH_3I showed that the rate of CH_4 production by the reaction $CH_3+CH_3I \rightarrow CH_4+CH_2I$ is independent of temperature from 40° to 100°C. and is decreased by added inert gas (CO_2). The same effects have been observed in other laboratories (18, 26) with the temperature range being extended to 315° and Ne, A, He, and CH_4 being shown to be effective as moderators. The quantum yield for the reaction of the hot CH_3 radicals with CH_3I is 0.003 (18, 25) for radicals formed by 2537 Å light and about 0.03 for 1849 Å light (18).

It has been observed that CH_4 and A do not reduce the quantum yield of the reaction of hot CH_3 radicals with CH_3I as much as they would if the energy of the CH_3 was all kinetic and could be lost by momentum transfer on collision (18). It is concluded that at least part of the energy must be vibrational. Apparently, light of 1849 Å contributes more to vibrational energy than 2537 Å since CH_4, A (18), and CO_2 [Hudson, Hamill & Williams

(26)] are all much more effective moderators at the higher wave length.

For hot methyl radicals formed by 2537 Å light the relative probability per collision that they will abstract hydrogen from CH_4, CH_3I, and CH_2I_2 has been observed to be 0.3:1:16. In an excess of CH_4 the quantum yield for the reaction with methane following light absorbed by $C^{14}H_3I$ is about 8×10^{-4} (18).

Martin & Noyes (21) have found that the presence of low mole fractions of oxygen during the photolysis of $Hg(CH_3)_2$ or CH_3I suppresses C_2H_6 production without suppressing CH_4 production to the extent that would be expected if thermal methyl radicals are responsible for the latter. Oxygen can remove thermal radicals before they have undergone the number of collisions required to encounter other methyls to form C_2H_6 or to acquire the activation energy for reacting with CH_3I or $Hg(CH_3)_2$, whereas, at the pressures used, the probability of an oxygen encountering a hot radical before the latter is thermalized is negligible. Within the limits of error the rates of methane formation were independent of temperature in the ranges studied.

In studies of the photolysis of $Hg(CH_3)_2$ in H_2, Phibbs & Darwent (20) have been led to postulate methane formation by hot methyl radicals ($CH_3+H_2\rightarrow CH_4+H$) because they observed a lower apparent activation energy for CH_4 formation below 100°C. than at higher temperatures, and because this low value was raised by added CO_2.

What appears to be a photochemical "hot molecule" reaction of excited I_2 molecules, $I_2+CH_4\rightarrow CH_3I+HI$, occurs when I_2 vapor in CH_4 absorbs 1849 Å light (18). Reaction by way of atoms is ruled out because iodine atoms produced by visible light do not react with CH_4 and because the kinetic energy of iodine atoms produced by 1849 Å is not great enough to meet the conservation of momentum requirement mentioned in the introduction to this section.

Hot reactions activated by nuclear processes in the gas phase.—If a mixture of I_2 vapor and CH_4 is irradiated with neutrons, iodine atoms with high kinetic energy, positive charge, and radioactively tagged, are produced by the I^{127} (n,γ) I^{128} (25 min.) process. About 45 per cent of these atoms react in a process of the type $I+CH_4\rightarrow CH_3I+H$ (22) which is about 50 kcal./mole endothermic and which is an inversion type reaction, in sharp contrast to the hydrogen abstraction reaction which occurs when photochemically produced Br or Cl atoms react with saturated hydrocrabons (e.g., $Br+CH_4\rightarrow CH_3+HBr$). Similar reactions (27) occur for iodine originally in the form of alkyl iodides and for Br_2 irradiated with neutrons in the presence of methane, ethane, and other hydrocarbons. Studies of these reactions in the presence of inert gases designed to moderate the high-energy halogen atom before it encounters a hydrocarbon molecule, and in the presence of additives of low ionization potential designed to neutralize it, have not yet given an unequivocal indication of the relative contributions of the charge and the kinetic energy to the reactivity but suggest that both may be necessary. Parallel studies on the reaction of bromine atoms produced by the isomeric transition,

Br^{80m} (4.4 hr.)→Br^{80} (18 min.) (average charge plus 10), show that they also undergo the inversion type reaction with methane.

Equally striking evidence for unique hot atom reactions has been obtained for chlorine in the irradiation of gaseous *n*-butyl chloride with neutrons. About 12 per cent of the Cl^{38} produced by the Cl^{37} (n,γ) Cl^{38} (38 min.) reaction appears as a compound which is higher boiling than butyl chloride, presumably a dichlorobutane, while essentially all of the remainder is in inorganic form (28). Again there must be an inversion reaction, splitting out a hydrogen atom, despite the low activation energy for hydrogen abstraction by chlorine atoms.

The evidence indicates that these gas phase hot reactions do not involve organic radicals but must occur in a one-step process on collision of the hot atom with the organic molecule. They are in contrast to the hot photochemical reactions cited above in that the products are different from those which would be produced by thermal atoms in the same systems.

Hot radical reactions in liquid and solid phases.—Hot radicals formed by ultraviolet or visible light would be expected to undergo reactions in the liquid phase similar to those in the gas. Hamill & Schuler (29) and Schuler & Chmiel (30) have given evidence for this type of reaction in the photolysis of CH_3I at 2537 Å. The latter authors find that the rate of CH_4 and C_2H_6 production is independent of both temperature and I_2 concentration in the ranges studied.

In contrast to most photochemically produced hot atoms, those produced by nuclear transformations or high-energy radiations may have sufficient energy to rupture molecules and produce radicals, in the slowing down process. If the hot radical comes to thermal energy in a solvent cage with a radical it has produced it may combine to form a stable product. This process, which requires the caging effect of the solvent, is experimentally indistinguishable from product formation by hot radical attack on a stable molecule. Investigations of these more complicated systems will be dealt with in later sections under the headings of Solid-State Effects, Activation by Nuclear Processes, and Radiation Chemistry.

Energy Transfer and Charge Transfer

The ultimate goal of the radiation chemist is to trace in detail the energy and charge transfer steps, and resultant chemical steps, of all types, which occur from the moment of passage of high-energy particles through a system until thermal equilibrium among stable chemical compounds is again achieved in the tracks of the particles. Because the primary action of radiation produces both ionization and excitation with many states of the latter being possible, and because there are many secondary physical and chemical acts which are in principle possible, including positive ion neutralization, negative ion formation, loss of energy by radiation, energy transfer by collision, decomposition to radicals, and decomposition to stable molecules, progress toward the goal is slow and must be taken a step at a time.

Electron capture by parent ion.—Much current thinking in the field tends to accept the point of view of Samuel & Magee (31) that in condensed phases positive ions are neutralized by rapid return to the parent ion of the electron removed from it by the ionizing radiation, though the point of view that the electron escapes from the parent ion also has strong support [Platzman (32)]. The assumption of prompt neutralization of the parent ion by its electron eliminates the necessity for considering charge transfer and negative ion formation processes in postulating mechanisms (33). An ingenious experimental test of the hypothesis has been attempted by Hamill & Williams (34) who irradiated dilute solutions of alkyl halides in hydrocarbons with γ-rays. Radioiodine was present to react with any alkyl radicals formed by electron capture by the halide in competition with return of the electron to the parent hydrocarbon ion (e.g., $CH_3I+e \rightarrow CH_3+I^-$, or $CH_3I^-+C_6H_{12}^+ \rightarrow CH_3+?$, followed by $CH_3+I_2^{131} \rightarrow CH_3I^{131}+I$). The authors interpret their results as consistent with the conclusion that the most efficient electron-capturing additives can compete effectively with the recapture by the parent ion when they are present at a mole fraction of about 10^{-3}, a value interestingly related to the estimate of Samuel & Magee that the electrons produced by ionizing radiation in water will undergo about 10^3 collisions with the solvent before return to the parent ion.

Transfer of electronic excitation from solvent to solute.—There are numerous examples in the literature wherein energy given to a solvent by γ-irradiation: (*a*) appears as fluorescent radiation from a low concentration solute; (*b*) causes decomposition of the solute out of proportion to the energy absorbed by the solute itself; and (*c*) is prevented from decomposing the solvent by the "protective action" of a solute. All of these must involve energy transfer from solvent to solute either by charge transfer, chemical action of free radicals, emission of radiation by the solvent and absorption by the solute, or transfer by collisions. Both physical and chemical experiments designed to show that the phenomena can be explained by collisional transfer have been reported during the last year. Furst & Kallman (35) have compared energy transfer and fluorescence yields in various xylene and cyclohexane solutions of anthracene, *p*-terphenyl, 9,10-diphenylanthracene, and naphthalene, excited by γ-rays, with the yields obtained from excitation by different wave lengths of ultraviolet light, the latter being of too low energy to cause ionization. The correlation between the two methods of excitation is evidence against energy transfer by ionization in the case of γ-excitation. Cohen & Weinreb (36) have shown that for dilute solutions of *p*-terphenyl in benzene, toluene, or xylene, where the solvent absorbs the 2537 Å activating light used, the *p*-terphenyl fluorescence is 20 times more intense than when a relatively transparent solvent such as chloroform is used. Related experiments on energy transfer in solutions of mixed phosphors under ultraviolet radiation have been reported by Germann *et al.* (37) and a discussion of different points of view which have been prominent in the field is given by Birks (38).

Burton & Patrick (39) have tested the suggestion that compounds such as *p*-terphenyl and anthracene (which are known to fluoresce in C_6H_6 solution as a result of energy transferred from the solvent when it is excited with γ-rays) may show a high protective effect in inhibiting the γ-ray decomposition of C_6H_6. An enhanced protective effect is not observed. This may be due to the fact that the induced fluorescence does not tap the excited states which lead to decomposition, or to the fact that the amount of energy tapped off is small compared to even the small amount which goes into chemical decomposition. In order to determine whether the protective effect (40) of added benzene in reducing the yield of volatile products from hydrocarbons under electron bombardment is due to preferential reaction of H atoms from the hydrocarbon with C_6H_6, rather than to energy transfer, Burton & Patrick (41) have bombarded cyclohexane containing C_6D_6 and analyzed for HD. The results of this work and related work by the same authors (33) on mixtures of propionaldehyde and C_6D_6 are consistent with a mechanism of protection by collisional energy transfer. In the latter work (33), C_6D_6 showed no protective effect on the radiolysis of propionaldehyde, a result consistent with the expectation that the excited states of lowest energy of the latter are lower than any in benzene. There was evidence for some sensitized decomposition of both cyclohexane and propionaldehyde by excited C_6D_6. In mixtures of cyclohexane, C_6H_6, and terphenyl, energy absorbed by the C_6H_{12} is transferred to the C_6H_6 and, in turn, to the terphenyl by collision processes, and finally appears as the emission spectrum of terphenyl [Burton & Berry (42)].

In a brief note Weiss (43) has dealt with theoretical considerations concerning the excitation of optical levels by ionizing radiation.

Stability of gaseous ions.—A gaseous ion formed by ionizing radiation is not usually neutralized by the electron which it has lost because the low density of the medium will allow the latter to escape the coulombic attraction of the parent. Such an ion may therefore have more opportunity to react with negative ions or molecules or undergo unimolecular decomposition. Rosenstock *et al.* (44) have sought to predict the fragmentation patterns of positive ions formed in a mass spectrometer. They assume that usually the newly formed excited molecule-ion does not decompose immediately but undergoes at least several vibrations, during which radiationless transitions result in distribution of the energy in a completely random fashion within the ion. Decomposition occurs when the nuclei are in proper configuration and a sufficient amount of energy has concentrated in the necessary degrees of freedom. The fragments may, in turn, decompose by a similar sequence. The authors present an absolute rate theory for isolated systems having a large number of degrees of freedom and obtain results in agreement with experiment in applying it to propane.

Although doubly charged ions are of minor importance in radiation chemistry, the mass spectrometric results of Mohler, Dibeler & Reese (45) on the rupture of such ions are relevant to the problem of interpreting the

rupture of the highly charged molecule-ions formed following isomeric transition of Br^{80m} in polyatomic molecules [for examples see (13)]. These investigators have determined the kinetic energy of the CH_3^+ fragments produced by the decomposition of 15 doubly ionized hydrocarbons in the mass spectrometer. In most cases the energy is very nearly equal to that predicted from the Coulomb repulsion between two positive charges separated by a distance equal to the length of the molecule.

Seven transitions of metastable negative ions formed by electron bombardment of $C_2H_5PO_2Cl_2$ have been observed in mass spectrometric studies by Donnally & Carr (46). The half-lives for the transitions $C_2H_5PO_2Cl_2^- \rightarrow PO_2Cl^- + (C_2H_5Cl)$ and $PO_2Cl^- \rightarrow Cl^- + (PO_2)$ have been found to be 1.9×10^{-6} and 4.8×10^{-6} sec., respectively.

Charge transfer cross sections.—Charge transfer cross sections between the ions N_2^+, O_2^+, O^+, and N^+, and N_2 and O_2 have recently been measured for ions in the range 9 to 250 ev by Potter (47).

Photosensitization by a solid.—A unique effect has been demonstrated by Grossweiner & Gordon (48) who find that both oxidation and reduction may be induced in $Fe^{++} - Fe^{+++}$ solutions by light which is absorbed by suspended HgS. There is a sharp decrease in effectiveness of the light at wave lengths above the photoconductive cut-off of HgS crystals, where the reflectance of the powder shows an abrupt increase. Oxygen is required for the oxidation reaction and strongly inhibits reduction while sodium chloride inhibits oxidation and enhances reduction. The highest efficiency observed was about one Fe^{++} ion oxidized per 300 incident photons.

Stopping power and ionization efficiency.—Comparison of the stopping power of liquid water for Po α-particles with that of the vapor at low pressure has been made by measuring the range in the vapor with and without a film of liquid water in the beam, the thickness of the film being determined simultaneously by optical means. The stopping powers were identical within the experimental error of 5 per cent [Ellis, Rossi & Failla (49)]. The ratios of ionization currents produced by three sources of widely different β-spectra, P^{32}, Th and S^{38} under identical conditions were essentially the same in seven gases N_2, O_2, CO_2, H_2, C_2H_2, C_2H_4, and CH_4 [Hersch (50)]. Gross (51) has measured the ionization currents produced in the same gases by a thin S^{35} β-source suspended in the center of an ionization chamber large enough so that all of the β-particles were stopped by the gas.

Radical Density Effects

Variation of radiation chemical yields with ionization density.—Ionizing radiation leads to the production of radicals in "tracks" and "spurs" rather than homogeneously distributed. The ultimate chemical effects of the radiation depend in part on the probability that these radicals will escape from each other rather than recombine. Densely populated radical tracks favor recombination. Allen & Schuler (52) have demonstrated that the use of cyclotron beams of He^{++} and H^+ ions provides a powerful tool for systematic

studies of such effects. By varying the energy of the beam they have varied the ionization density at the point of entrance of the particles to the irradiated medium from 5 to 0.5 ev/Å. Over this range the oxidation yield for 1 mM Fe^{++} in 0.8 N H_2SO_4 rises continuously from about 6 to 12 molecules oxidized per 100 ev absorbed. Continued rise toward the value of 15.5 obtained with the very low ionization density produced by 2 Mev electrons is indicated. Data of other workers (53, 54) for the oxidation of Fe^{++} solutions when irradiated with α-particles from Po fit well on the same curve. In sharp contrast, the 100 ev yield for production of H_2 from cyclohexane is independent of ionization density over the same range, and equal to that for 2 Mev electrons (52), indicating a great difference in the mechanisms of radiolysis in the aqueous and organic systems.

Primary quantum yield of photodissociation.—It has been recognized for many years (55) that when a molecule in a liquid absorbs a light quantum of sufficient energy to dissociate it the potential fragments may not escape from each other, either because they are held in proximity by the solvent cage while the energy of dissociation is transferred to the solvent, or because of diffusive recombination after very temporary escape. Similar considerations are of importance in radiation chemistry. Only recently have quantitative data become available.

Using the flash photolysis technique, Marshall & Davidson (56) have obtained a value of 19 per cent for the fraction of I_2 molecules which dissociate in CCl_4 solution when they absorb visible light which would dissociate them 100 per cent of the time in the gas phase, and a value of 14 per cent has been obtained independently (57) by similar methods. In striking agreement with these values is the value of 14 per cent obtained by Lampe & Noyes (58) by a chemical method in which they used a scavenger to react with the iodine atoms which escape from each other. These authors show that the quantum yield for escape decreases with increasing molecular weight for the three solvents hexane, carbon tetrachloride, and hexachlorobutadiene, the observed values being 66 per cent, 14 per cent, and 8 per cent, respectively, at 25°C. The value for hexachlorobutadiene increases from 4 per cent to 15 per cent with increase in temperature from 15° to 35° and a positive temperature coefficient is also observed for the other solvents.

Determination of radical distribution.—If the reactive fragments produced by radiation combine with other fragments from the same track or with molecules of the medium the rate of product formation and the nature of the products is independent of the intensity of the radiation. A variation in the type of products with intensity or a variation in rate of product formation other than first-order with respect to the intensity would indicate that reactive fragments from one track were reacting with those from another, although lack of such variation is not conclusive proof of the absence of such interaction. No such intensity effects have been observed in the case of reactions activated by nuclear processes (13) and, in general, none are observed for activation by ionizing radiation. In those cases where there is a depend-

ence on intensity other than first power there is a possibility of determining the radical lifetime by the use of intermittent radiation in bursts of variable frequency. Examples of this technique are given by Brasch, Huber & Waly (59), and by Spinks and co-workers (60, 61, 62).

The use of scavengers for free radicals has proved to be revealing as to the fraction, and in some cases the identity, of the radicals which escape from their parent hot spots in reactions activated by nuclear transformations (13). Hart & Walsh (63) have shown that Cu^{++} may be used to cancel out the effect of radical reactions in the oxidation of Fe^{++} induced by γ-rays in $0.8N$ H_2SO_4, leaving as a residual reaction only that due to "molecular products." Continuing earlier work on diphenylpicrylhydrazyl as a radical scavenger in organic solutions, Chapiro (64), has investigated the spatial distribution of primary radicals as a function of γ- and x-ray intensity. The assumption is made that the concentration of DPPH necessary to capture all of the primary radicals is equal to the local concentration of radicals. In addition to these examples, many other investigations have been made in the year under review, particularly in aqueous systems, to distinguish reactions of radicals which escape prompt recombination from radical or molecular reactions which occur at the site of excitation. Reference will be made to them later.

Theoretical treatment of diffusion kinetics.—Reactions with very low activation energy, such as those between free radicals, are diffusion controlled. An understanding of the variables which control the probability that radicals produced in pairs, in spurs, and in tracks of varying radical density will encounter each other and react is important for the quantitative elucidation of many photochemical, radiation-chemical, and nuclear-transformation-induced reactions. Since, in most cases, neither the initial distribution of radicals, nor the values of the parameters controlling their diffusion and reaction are known with certainty it is necessary to set up an assumed model as a basis for the mathematical treatment. The restrictions brought out by the mathematical treatment serve as a guide in interpretation of data, and comparison of the data with predictions serves to evaluate the plausibility of the model. Several relevant papers on diffusion kinetics have appeared in the last few years. Collins & Kimball (65, 66) showed that the fundamental concepts of the theory of the kinetics of colloid coagulation as developed earlier by Smoluchowski are applicable to bimolecular processes in general and pointed out that the knowledge that a particle has not reacted within a time t diminishes the probability of a potential reactant being in the neighborhood. Samuel & Magee (31) set up models describing the geometrical effects in water as a result of diffusion of radicals from tracks of high-energy β-particles, low-energy β-particles, and α-particles. The calculated relative rates of reactions which occur by prompt reaction of radicals in the track relative to reactions of radicals which have diffused, agree well with experiment. Noyes (67) has calculated that two iodine atoms separated by one molecular diameter in hexane at 25°C. have a 50 per cent probability of combining with each other within 10^{-6} sec. In a later paper (68), he has

dealt extensively with the theory of diffusion controlled reactions involving reactive molecules or pairs of molecules produced at random throughout a system, with particular emphasis on the time dependence of the reactivity of a molecule in such a system.

A simple model of the competition between scavengers and alkyl radicals for halogen atoms produced by the Szilard Chalmers (n,γ) process in alkyl halides has been treated by Roy, Williams & Hamill (69) by the methods suggested by the work of the above authors. They obtain satisfying agreement with experiment. Such agreement demonstrates that this method of treatment of the data does not exclude the reaction model used. On the other hand, such agreement may be fortuitous and the true reaction situation more complex than suggested.

Solid-State Effects

From the point of view of molecules or radicals which have been activated by ionizing radiation or nuclear transformation, a solid differs from the same compound as a liquid because of the differences in: (*a*) orientation of the molecules, (*b*) density, (*c*) mobility of the molecules. The first and second differences may affect the primary decomposition yields and products from ionized or excited species by altering the relative probability of transfer of electronic energy, radiation, collisional loss of vibrational energy, and dissociation. The second and third may favor stronger caging effects and hence more primary recombination of radicals. The mobility of molecules may be so low that radicals (or electron traps in polar media) are "frozen-in" and do not react or combine until the temperature is raised.

Only a little work has been done on the chemical effects of radiation on simple organic solids or on the comparison of such radiation effects on the same compound in the liquid and solid phases. More investigation along these lines should provide clues both as to the effects of phase on chemical reactions in general and as to the nature of the elementary processes of radiation chemistry.

"Frozen-in" radicals and excited states.—Evidence for the "freezing-in" of photochemically produced C_2H_5 and I radicals has been provided by Norman & Porter (70), who showed that there is no coloration produced when a dilute solid solution of C_2H_5I in hexane is irradiated at -195°C. with ultraviolet light, but that if the solid is warmed following irradiation, I_2 color appears. Similarly, when a solid solution of I_2 in hexane is irradiated the I_2 color fades as a result of the conversion of I_2 molecules to colorless frozen-in I atoms, but returns when the system is warmed sufficiently for the atoms to diffuse to each other. Using the same technique, the authors have observed the absorption spectra of CS and ClO radicals for many hours after the photolysis of solid solutions of CS_2 and ClO_2, respectively. In work from the same laboratory (71) using flash photolysis techniques, the half-lives and extinction coefficients of metastable triplet states of anthracene and many other compounds in liquid hexane and other solutions have been measured.

The half-lives are in the range of 10^{-5} sec. as compared to the much longer lifetimes of phosphorescence in the solid state observed by earlier workers, indicating that the molecular situation in the solids is less favorable to de-excitation of the electronic states than is that in the solutions.

Mador (72) has observed that 0.1 mm. thick films of CH_3I subjected to 10^{19} quanta/cm.^{2} of 2537 Å light at 4°K. develop a red color which may be due to CH_3 radicals, and on warming to 40°K. disintegrate violently in a manner which is attributed to exothermic radical recombination reactions. A similar violent release of stored energy, following irradiation of acrylamide and related monomers with γ-rays at −18°C., has been reported by Mesrobian and co-workers (73). When the samples were heated to room temperature following irradiation, polymerization proceeded rapidly, heating the sample sufficiently to cause it to "explode." Mador & Williams (74) have decomposed HN_3 by an electric discharge, freezing out the products at 4°K. The solid obtained gave absorption bands attributable to NH and NH_2.

Interesting evidence on reactions of trapped radicals produced by the $C^{12}(\gamma,n)C^{11}$ reaction in anhydrous Na_2CO_3 has been obtained by Sharman & McCallum (75). When the crystals are dissolved in water following γ-irradiation the C^{11}, which can be identified by its radioactivity, is distributed percentagewise as follows: CO_2, 22; CO, 0.01; HCOOH, 0.03; $(COOH)_2$, 39; $HOOCCH_2OH$, 24; and HOOCCHO, 10. If, however, the crystals are heated before dissolving the percentages of C^{11} activity present as glyoxylic, glycollic, and oxalic acid decrease, each at a different temperature (in the range from 100° to 500°C.), and the corresponding activity appears instead as CO_2. The results may be interpreted to mean that the recoiling C^{11} forms several kinds of radicals which are stable within the crystal at room temperature. These react with water to give the observed complex products, and have different activation energies for reacting within the crystal at elevated temperatures to form CO_2.

It is probable that trapped radicals which react with water on dissolution of the crystal likewise account for some of the C^{14}-containing products which result from the $N^{14}(n,p)C^{14}$ process in NH_4Br [Yankwich & Vaughan (76)], and in $(NH_4)_2SO_4$ [Yankwich & Cornman (77)]. These authors have been able to show the formation of nine C^{14}-containing compounds from NH_4Br and seven from $(NH_4)_2SO_4$, in addition to CO, CO_2, and HCN.

Yields in organic solids.—When alkyl halides are irradiated with neutrons the halogen atoms which capture neutrons emit a γ-ray and recoil with high energy, splitting the parent bond, and rupturing bonds in adjacent molecules. They eventually enter stable combination, some by hot reactions and some by thermal reactions. The fraction which reenters organic combination is known as the "organic yield." The ratio of the organic yield in the liquid phase to that in the solid has been determined for some 20 alkyl chlorides, bromides and iodides [see pp. 203 and 216 of ref. (13)]. The ratios range from slightly above one to much less, with no apparent relationship to the structure of the halide or to the density change on freezing. In some cases the

yield in the solid phase is independent of temperature, while in others it is temperature sensitive.

Data on the effect of phase on the rate of I_2 production during irradiation of five alkyl iodides (78) with Co^{60} γ-radiation show no apparent correlation with the (n,γ) results, although exhibiting independently interesting phase effects. The ratios of the rates of iodine production from crystalline CH_3I, C_2H_5I, i-C_3H_7I, and n-C_4H_9I at $-190°$C. to the rates in the liquid at 25° are about 0.25, 0.20, 0.11, and 1.1, respectively. Of particular interest is the fact that the rate in the solid *glass* at $-190°$ is approximately twice that in crystals at the same temperature for both C_2H_5I and i-C_4H_9I, the two cases where such a comparison was made. The rate of production of I_2 in liquid C_2H_5I is independent of temperature from 108° to $-78°$C. The results seem to indicate that the use to which the energy furnished by the ionizing radiation is put is strongly conditioned by the orientation of the molecules in the solid state.

The radiolysis of CCl_3Br with Co^{60} γ-rays has been studied (79) in the solid, liquid, and gas phases, from $-190°$ to 117°C. There is no change in the rate of Br_2 production at the melting point ($-5.6°$) or at a solid phase transition which occurs at $-35.5°$C. The rate is independent of temperature below about $-78°$ but increases with temperature with an apparent activation energy of about 2 kcal./mole above $-78°$.

Paramagnetism, fluorescence, and thermoluminescence.—Smaller, Matheson, & Yasaitis (80) have observed paramagnetic resonance peaks induced in both H_2O and D_2O by γ-radiation at 78°K. and measured at 78°K. and 4°K. These remain at 108°K. but disappear at 123°K. Work from the same laboratory [Grossweiner & Matheson (81)] has shown that the x-ray irradiation of ice induces a fluorescence with an efficiency of about 10^{-5} quanta emitted per ion pair formed, which increases to the saturation intensity at a rate which is first order with respect to time of irradiation. The saturation intensity decreases with increasing temperature. The fractional build-up to maximum intensity is retained during periods in the absence of x-irradiation at 78°K. but decays away slowly at 130°K. and very rapidly at 175°K. The build-up is ascribed to a production of "active luminescent centers" by the trapping of thermal electrons by hydrated impurity cations, followed by subsequent relaxation of the dipole sheath. The free atoms so formed may be ionized by energetic electrons and then emit light as they capture other electrons. Ice at low temperatures shows no phosphorescence following its fluorescence but exhibits a thermoluminescence with a peak at 155°K.

Catalysts.—To test the hypothesis that changes produced in ionic crystals and semiconductors by ionizing radiation might affect catalytic behavior, Taylor & Wethington (82) have investigated the effect of γ-ray irradiation of ZnO on its catalytic activity for the hydrogenation of C_2H_4. The catalytic activity was lowered, either as a result of electronic changes or of poisoning by polymerization of residual C_2H_4 on the surface.

NaOH.—Hochanadel (83) has shown that fused NaOH is very stable to irradiation by 1.3 Mev electrons, giving less than 4×10^{-4} molecules of H_2 per 100 ev absorbed.

Activation by Nuclear Transformations

In this section, recent work on chemical effects of nuclear transformations not referred to in preceding sections, will be summarized. Emphasis will be placed on certain significant new developments, while others, which may be equally important, will be treated more briefly because of the limited space available. An introduction to this field and references to earlier work are given in a previous review article (13).

Labelling of complex molecules.—Of both practical and theoretical interest are recent demonstrations that a usable efficiency may be achieved in radioactively tagging aliphatic and aromatic hydrocarbons and sugars with the aid of hot atoms produced by nuclear processes.

Neutron irradiation of a 5 mole per cent solution of aniline or methyl amine in *n*-pentane leads to 25 per cent of the C^{14} from the $N^{14}(n,p)C^{14}$ process as *n*-C_5H_{12}, 1 per cent as *i*-C_5H_{12}, 12 per cent as *n*-C_6H_{14}, 6 per cent as other hexanes and 39 per cent as higher boiling hydrocarbons [Schrodt & Libby (84)]. Anthracene-C^{14} has been produced in 0.2 per cent yield by neutron irradiation of its nitrogen homologue, acridene, while 3 per cent of the C^{14} was found as acridene [Wolf & Anderson, (85)].

Using a process which they term "heterogeneous recoil tagging," Wolfgang, Rowland & Turton (86) have subjected finely ground mixtures of $LiCO_3$ with glucose to neutron irradiation to produce the $Li^6(n,\alpha)T^3$ reaction. The diameter of the $LiCO_3$ particles was about 1 μ and the range of the tritons is about 50 μ in organic material. About 10 per cent of the tritons stopped in the organic phase were incorporated into nonlabile positions in glucose, giving a specific activity of about 2 μc./gm. This remained essentially constant through five recrystallizations as the penta-acetate. Specific activities 100-fold higher appear practicable for glucose, with still higher levels possible for compounds less sensitive to radiation decomposition. The same authors (86) report that in an independent check of this labelling technique Kaplan has found that 25 per cent of all the tritons produced in a mixture of Li_2SO_4 and benzoic acid result in benzoic acid labelled in the ring hydrogens, 96 μc./gm. being obtained with little radiation decomposition.

While reactions of the type described above seem not implausible in terms of existing theories (13) of activation by nuclear processes it is difficult to conceive that the $Co^{59}(n,\gamma)Co^{60}$ process on the Co of vitamin B_{12} ($C_{61-64}H_{86-92}N_{14}O_{14}Co$) can produce Co^{60} in this hexacovalent coordination complex. It is, therefore, reassuring that two groups of workers (87, 88), using careful countercurrent distribution techniques for separation of the vitamin from their irradiated samples, have found no evidence for such tagging, in contrast to the work on this problem discussed in an earlier review

(13). In view of the experiments reported above, however, it would seem that there may be some hope of tagging complex biologically important molecules with C^{14} or H^3.

Maddock & Sutin (89) have irradiated crystalline $(C_6H_5)_3As$ with neutrons and found As^{76} in the form of $(C_6H_5)_3As$, phenylarsine oxides, phenylarsonic acids and arsenate.

Neutron energy effects and isotope effects.—Capron and co-workers (90) have reported that the organic yields of Br^{80m} and Br^{80} produced by the (n,γ) process in organic bromides differ, and have ascribed the difference to differences in the initial energy of the two species. These investigators used reagents which were not especially purified. More recent work (91) indicates that the yields of Br^{80m}, Br^{80}, and Br^{82} are indistinguishable when highly purified materials are used, while confirming the fact that differences in yield can be reproduced with unpurified reagents.

A striking demonstration that the initial energy of the recoil particle does not influence its final chemical combination has been given by Schuler (92), who showed that I^{128} and I^{126} atoms produced in methyl and ethyl iodides with kinetic energies in excess of 100,000 ev by the $I^{127}(d,p)I^{128}$, $I^{127}(n,2n)I^{126}$, and $I^{127}(\gamma,n)I^{126}$ processes give organic yields indistinguishable from those which have been observed for the same compounds with iodine atoms of very much lower energy produced by the (n,γ) process (93). A similar comparison of organic yields for atoms produced with widely different energies in crystalline organic halides would be desirable to test the suggestion (94) that the observed difference in organic yield of Br^{82} and Br^{80m} in crystalline propyl bromide is due to differences in the initial kinetic energies of the atoms.

Scavenger investigations.—Considerable interest centers in the question as to which products of a reaction activated by the (n,γ) process are produced in hot processes (not susceptible to competition by radical scavengers) and which by thermal processes. This question has been investigated earlier for CCl_3Br (95), where it was demonstrated that the organic yield of the parent product was reduced most by scavengers and also that certain products may be increased by a scavenger which can compete with bimolecular radical-radical reactions. It has now been studied for more complex molecules (96), the propyl bromides, by examining the organic yields of eleven products with and without 5×10^{-2} molecule fraction of Br_2 present during the irradiation. Some products are formed almost exclusively in the hot volume, i.e., before the tagged atom enters thermal equilibrium with the medium, These include those which are formed by combinations of the atom with two or more radicals (hexyl bromide) and those formed by hydrogen replacement (dibromopropanes). Most of the other types of products examined are produced by both hot and thermal processes.

Roy, Williams & Hamill (69) have extended earlier evidence (97) on the effect of 1,2-dibromoethylene and Br_2 on the organic yield of the (n,γ) reaction on C_2H_5Br by using these two scavengers in competition with each other. They have also reported results of a few measurements designed to test the

effect of temperature on the ability of $C_2H_2Br_2$ to scavenge thermalized bromine atoms in competition with the reaction of these atoms with solvent molecules to form HBr. Since the scavenging action (exchange of Br with $C_2H_2Br_2$) is presumed to have an activation energy near zero and the HBr formation much higher, an increase in temperature should decrease the effectiveness of the scavenger. The limited data are consistent with this conclusion.

Hamill & Williams (98) have found, in agreement with other work (28), that Cl_2 reduces the organic yield of the $Cl^{37}(n,\gamma)Cl^{38}$ reaction in CCl_4. This is in contrast to the notable absence of such an effect in hydrogenous hydrocarbons (28) where tagged Cl atoms can react with the solvent to form HCl with very low activation energy. Added allyl chloride has been shown (98) to raise the organic yield of the Cl^{38} in CCl_4 from circa 40 to 53 per cent.

It has been shown (99) that, as would be expected, I_2 is as effective a scavenger as Br_2 (97) in reducing the organic yield of Br^{80m} from the (n,γ) process on either C_2H_5Br or CCl_3Br. Recently published results of Brustad & Baarli (100) on the effects of purification, I_2 concentration, and temperature on the yields and products of the $I^{127}(n,\gamma)I^{128}$ process in CH_3I are, in some respects, in qualitative agreement with previous work (93), and in other respects in sharp disagreement. Where there is disagreement, the validity of the results is questionable in view of the agreement between other laboratories (92, 93).

Effect of γ-radiation on organic yields from (n,γ) activation.—It is known (ref. 13, p. 216) that wide variations of γ-ray intensity and total dose during neutron irradiation do not alter the organic yields from alkyl halides, within the low ranges used in most studies of the chemical effects of the (n,γ) process. Recent work (101) shows, however, that the organic yields of Br^{82} (36 hr.) and Br^{80m} (4.4 hr.) in purified degassed *n*-propyl bromide increase with increased γ dosage in excess of about 2×10^4 r, the Br^{82} yield increasing faster than that of Br^{80m}. The increase must be due to olefin-like impurities produced by the radiolysis of C_3H_7Br. These react in a slow process with the tagged inorganic products (Br_2 or HBr) of the (n,γ) process to return them to organic combination. Since the average lifetime of the 36 hr. species in the solution is greater than the 4.4 hr., its organic yield is more sensitive to impurities. Consistent with this reasoning is the observation that the Br^{80} (18 min.) organic yield does not rise until a γ-dose of more than 2×10^5 r. has been received. A much higher γ-dose can be "tolerated" in the presence of oxygen, presumably because it scavenges radicals which would otherwise form the olefin-like substances.

Reactions of I and Br activated by nuclear processes in liquid hydrocarbons.—Earlier work (97) indicated that the organic yields of the tagged halogens form the (n,γ) reaction on alkyl iodides increase with increasing dilution with hydrocarbons, and with increasing chain length of the normal paraffin hydrocarbons used as diluents. These facts have now been confirmed (99) for C_2H_5I and C_2H_5Br in the series from pentane through decane. By the use

of halogen scavengers it has been shown that the increase with increasing chain length is due primarily to hot processes (i.e., not susceptible to scavenger interference). Of particular interest is the fact that the organic yield in the dilute hydrocarbon solutions decreases with increase in temperature. The organic yields of the isomeric transition of Br^{80m}, like those from the (n,γ) process, increase with dilution with hydrocarbons and with chain length. They vary with the nature of the Br^{80m}-containing compound, increasing in the order: Br_2, $CHBr_3$, CCl_3Br (99).

Reactions of aromatic compounds with halogen atoms activated by the (n,γ) *process.*—Gavoret & Ivanoff (102, 103, 104) have investigated the (n,γ) activated reactions of Br in nitrobenzene, methyl and ethyl benzoates, benzene and toluene, with an aim toward determining substitution ratios between different compounds, and the ratio of *ortho*, to *meta*, to *para* substitution. They interpret their results as giving information as to whether the atoms are thermalized and whether they are charged at the time of entering organic combination.

Products of the (n,γ) *process in salts and metal complex compounds.*—A number of investigations of the valence states of metal atoms which have undergone the (n,γ) process in salts or complexes have been made since the last review (13) on chemical effects of nuclear transformations. These include studies of permanganates by McCallum & Maddock (105), of K_2CrO_4 by Green, Harbottle & Maddock (106), of various crystalline Cr compounds by Harbottle (107), of Cr^{+++} and $CrO_4^{=}$ solutions by Harbottle & Fishman (108), of Re salts by Herr (109), and of organic Pt complexes by Haldar (110).

Bond rupture as a result of β*-decay of* Pb^{210} *in* $Pb(CH_3)_4$.—Edwards, Day & Overman (111) have determined the fraction of the Bi^{210}, formed by β-decay of Pb^{210} in $Pb(CH_3)_4$ which is nonvolatile. The volatile fraction is assumed to be $Bi(CH_3)_3$, and the nonvolatile to represent further rupture of the bonds in the parent molecule. Rupture is presumably the result of the positive charge produced by internal conversion and Auger processes. The results indicated 5 to 10 per cent failure of bond rupture in the gas phase and 50 per cent in liquid $(PbCH_3)_4$. When the pure liquid was diluted with C_6H_6, CCl_4, or C_8H_{18} the percentage rupture failure rose to a maximum of 82 per cent at 0.05 mole fraction and then fell abruptly to 10 per cent at still lower concentrations. This maximum in bond rupture with increase in concentration at very low concentrations awaits an explanation.

Charge produced by nuclear transformations.—Highly relevant to the interpretation of the chemical effects of nuclear transformations is a knowledge of the charge produced on the atom by the transformation. Perlman & Miskel (112) have reported that the average charges on Cl^{37} and Xe^{131} produced by the $A^{37} \xrightarrow{e^-\ \text{capt.}} Cl^{37}$ and $Xe^{131m} \rightarrow Xe^{131}$ processes, are $+3.41 \pm 0.14$ and 8.5 ± 0.3, respectively. Wexler (113) has observed the following: T_2, β^- decay, $+0.9 \pm 0.1$; $C^{14}O_2$, β^- decay, $+1.0 \pm 0.2$; A^{41}, β^- decay,

$+1 \pm 0.1$; $C_2H_5Br^{80m}$, I. T., $+10 \pm 2$; Kr^{83m}, I. T., $+7.7 \pm 0.4$; A^{37}, e^- capt., $+3 \pm 0.2$.

In seeking to interpret the chemical effects of the isomeric transition of Br^{80m} which have received considerable study, it would be useful to know the fraction of the atoms having each possible charge. This has not been determined but data of this type have been obtained by Kofoed-Hansen (114) for the Cl^{37} atoms produced in e^- capture by A^{37}. He finds the following percentages for the charges indicated: +1, 26; +2, 13; +3, 38; +4, 18; +5, 4; +6, 1.

Johnston & Arnold (115) have sought to check on proposals that the rather high failure of bond rupture following isomeric transition reported for HBr is due to the stability of HBr^{+z} ions with Z greater than 2. Using a mass spectrometer with ionizing energy which produced good yields of Br^{+3} and Cl^{+3} they have found no HCl^{+3} or HBr^{+3} and conclude that these and more highly charged molecular ions must have lifetimes shorter than 30 μsec.

Radiation Chemistry

The object of this section will be to survey briefly work in radiation chemistry during the year under review, which has not been discussed above.

Gases.—By observing the effects of electrical fields on the chemical yields of gas phase radiolysis reactions, Essex and co-workers have been able to obtain information on the importance of ion combination processes. These and related methods used in a series of investigations to determine the relative importance of four probable primary reaction steps are discussed in a recent paper (116).

Using the β-particles of tritium as the activating radiation, Dorfman & Shipko (117) have found that in $T_2-C_2H_2$ mixtures C_6H_6 is the only volatile product. The 100 ev yield for disappearance of C_2H_2 (to form cuprene and C_6H_6) is 71.9, and that of C_6H_6 formation is 5.1. Two different excited states of C_2H_2, one leading to cyclization and one to polymerization are suggested to account for the fact that a constant fraction (0.21) of the C_2H_2 forms C_6H_6 regardless of a 5-fold variation in C_2H_2 pressure and a 20-fold change in radiation intensity. Dorfman & Hemmer (118), also using T_2 as the activating source, have found the $H_2+O_2 \rightarrow H_2O$ reaction to be directly proportional to the T_2 concentration, and independent of a considerable change in O_2 pressure, with no evidence for H_2O_2 formation. The 100 ev yield of H_2O is about 10.

When the decomposition of NH_3 is studied in a d.c. electric discharge at 0.6 to 11 mm. pressure the primary chemical effects result chiefly from low excited states of NH_3 with energies far less than required for ionization and probably below optically attainable levels. Devins & Burton (119) report that in such a system N_2H_4 and $N_2(+H_2)$ are produced in apparently unconnected processes, the latter being formed uniformly throughout the discharge while the former is produced mainly in the positive column. The 100 ev yield of N_2 is about 0.8 and that of N_2H_4 is $\geqq 2.4$.

Other gas phase studies include investigations of NO_2 by Harteck & Dondes (120), and of the effects of irradiation on the effectiveness of combustion of hydrocarbons by Cullen & Gluckstein (121).

Aqueous systems.—Because of their biological importance and their use in nuclear reactors and in dosimeters, water and aqueous solutions continue to outrank all other materials in the time devoted to their study by radiation chemists. The published work of the last year alone is so extensive as to preclude more than brief summary treatment in this chapter. The previous volume of this series ably reviewed the subject (11); several other good discussions of current evidence and points of view in the field have appeared within the last two years (122 to 125); it is to be expected that a review by Dainton (126), scheduled to appear soon, will deal with the subject in detail; and Allen (127) has surveyed the radiation chemistry of water with particular reference to its importance in reactor technology.

Good discussions of the primary physical processes by which radiation loses its energy to water have been provided by Platzman (5, 32), and Fröhlich & Platzman (128). In addition to considering the loss of electron energy by excitation and ionization, these authors point out that an appreciable fraction must be lost to dipolar relaxation, that is to heat. They have also pointed out that the Franck Condon principle excludes the possibility of an electron reacting rapidly (10^{-13} sec.) with a water molecule, and that such interaction can only take place after it has had opportunity to become thermalized and hydrated (10^{-11} sec.) (32). (It has been mentioned above that the estimates of Samuel & Magee (31) favor the return of the electron to its parent ion within 10^{-13} sec.) Platzman & Franck (129) have dealt with the role of hydration configuration in electronic processes involving ions in aqueous solution. Laidler (130) has constructed schematic potential energy diagrams of the excited states of H_2O, H_2O^+, and H_2O^- which may decompose to H, O, H_2, OH, H^+, H^-, O^+, OH^+, and H_2^+.

Although most investigators now ascribe a prominent role in the radiation chemistry of water to H radicals, Hassinsky & Lefort have prepared an extensive review (125) of evidence which leads them to the conclusion that its role is minor relative to that of OH. Laidler points out that the scheme which he has formulated (130) by a consideration of the excited states of gaseous molecules is consistent with this and Barron (131) raises similar questions based on observations in biological systems. Recent workers (132) have stressed the fact that highly refined experimental techniques, with great care to avoid impurity effects, are necessary to give satisfactory data for use in resolving problems of the type raised by Haissinsky & Lefort (125).

Many of the recent experimental investigations of the radiolysis of aqueous systems have been concerned with: (*a*) distinguishing quantitatively the "molecular yield" (resulting from excited molecules, or from radicals which combine immediately after birth) from the "radical yield" (attributable to radicals which escape from their site of birth); and (*b*) with the detailed elucidation of the reactions of radicals with each other, with the solvent,

with products, and with added solutes. These investigations include determinations of the molecular hydrogen yield from the γ-irradiation of various alkaline and neutral solutions [Schwarz, Losee, & Allen (132)]; the radical pair yield in H_2SO_4 solutions of $Ce(SO_4)_2$ as deduced from the rate of Ce^{+4} reduction in the presence of CO, H_2, N_2, and He [Johnson & Weiss (133)]; the H_2O_2 yield in the γ-irradiation of air-saturated H_2O [Allen & Holroyd (134); Ghormley & Hochanadel (135)]; and the radical yield from H_2O [Rowbottom (136)]. Kelley, Rigg & Weiss (137) have compared the observed ratio $[HDO][H_2]/[H_2O][HD]$ for hydrogen produced by x-rays on deuterated $FeSO_4$ solutions with and without ceric sulfate added, with that calculated from the equilibrium constant, and that obtained by photochemical activation. They interpret their results as evidence that the molecular yield of H_2O_2 occurs by reaction between two excited H_2O molecules rather than by an avenue which would allow H atoms to come to exchange equilibrium with the medium.

Hart has reported new data on the use of γ-irradiated aqueous formic acid-oxygen solutions for the determination of molecular product and free radical yields. The effects of oxygen concentration over a wide formic acid concentration range (138) and of pH (139) are shown. Among the interesting conclusions are the value of 540 for the ratio $k_{(H+O_2)}/k_{(H+HCOOH)}$ and the indication that at high HCOOH concentrations the latter may compete with H_2O in capturing electrons.

Studies dealing with the radiation-induced oxidation of Fe^{++} include those of Schwarz (140), who finds a temperature coefficient for the oxidation of only 0.04 ± 0.03 per cent per degree, in contrast to 0.2 and 0.4 found by previous workers, and who points out how impurities may have led to high values; Hart & Walsh (63), who show that Cu^{++} lowers the yield, $G_{Fe^{+++}}$, from 15.6 to 0.64, presumably by cancelling the effects of HO_2 and OH radicals; Miller & Wilkinson (54), who have studied the oxidation, induced by Po^{210} α-particles as a function of the Fe^{++} concentration, pH and the presence of air (they, like authors mentioned above (125, 132, 139), consider the possible significance of the $H+H^+$ reaction); Vermeil & Cottin (141), who report that Fe^{++} is not oxidized and Fe^{+++} is reduced by γ-irradiation of deaerated aqueous solutions of the ions containing cyclohexane, butanol, or cyclohexanol, while a radiation-chemical equilibrium between Fe^{++} and Fe^{+++} is achieved in the presence of C_6H_6. Barr & King (142) compared the rates of oxidation of Fe^{++} in the presence and absence of oxygen.

Studies of aqueous systems containing other ions include work on the radiation chemistry of NO_2^- solutions, where competition between H_2O_2 and NO_2^- for H atoms is believed to be a main feature of the mechanism [Schwarz & Allen (143)]; the effect of Br^- on the H_2O_2 yield from the γ-irradiation of H_2O [Sworski (144)]; the inhibiting action of Cl^- on the formation of H_2O_2 by Po α-rays [Anta (145)]; the oxidation of $PO_3^{\equiv}$ by Po α-rays [Cottin (146)]; the production of I_2 from solutions of KI by x-rays [Johnson (147)]; and the α-ray induced chain reaction leading to oxidation of oxalate

to CO_2 in $HgCl_2$ solutions [Hausman & Davis (148)]. Scholes & Weiss (149) have discussed the degradation of aqueous nucleic acid by x-rays under various conditions; Fiquet & Bernas (150) attempted to detect H radicals from the radiolysis of H_2O by looking for C—D bonds in the infrared spectra of polymers formed by irradiating solutions of monomers in D_2O; Rolin (151) has compared the gaseous products from pile irradiation of pure degassed water with the products when the water contained dissolved organic compounds and Mohrs salt; Phillips (152) has investigated the effect of 1 Mev electrons on aqueous carbohydrate solutions; Ebert & Alper (153) have determined the H_2O_2 content of irradiated solutions, and the inactivation of bacteriophage as a function of H_2O_2 present; and Lefort (154) has discussed the action of α-rays on aqueous solutions.

It is interesting to note that ultrasonic irradiation of water produces a steady-state concentration of H_2O_2, that hydrogen is produced at a rate which is reduced in the presence of oxygen, and that other analogies exist between the decomposition of water by ionizing radiation and ultrasonic radiation (155).

Organic liquids.—Perhaps the single most important experiment related to the mechanisms of radiolysis of organic liquids which has been reported in the period under review is the demonstration, referred to in an earlier section, that the H_2 yield for the radiolysis of C_6H_{12} is independent of the ionization density in the track of the ionizing particle [Allen & Schuler (52)]. It will be of much interest to see whether other products of this radiolysis and products of the radiolysis of different organic compounds behave in the same manner.

Other significant observations include the fact that I_2 yields from the radiolysis of liquid alkyl iodides increase with increasing number of H atoms on carbon atoms adjacent to the C having the C—I bond [(78); Cochran, Hamill & Williams (156)]. A similar increase occurs for the photolysis of the alkyl iodides in the pure state but does not occur for their solutions in hydrocarbons (156). Photolysis of C_2H_5I in paraffin oil yielded H_2, C_2H_4, C_2H_6, and I_2 in the ratio 11.8:26.7:10.9:18.5. When deuterated C_6H_{14} was the solvent 20 per cent of the hydrogen was HD, emphasizing the fact that the solvent cannot be considered as inert in such processes (156). The results are in keeping with the conclusions that similar radical species are formed in the photolysis and radiolysis and that hot radicals play an important role. The x-ray-induced reactions of solutions of I_2 in n-C_7H_{16} have been studied by Forsyth, Weber & Schuler (157) for the primary purpose of determining the usefulness of I_2 in the determination of free radical production in liquid hydrocarbons. The reaction is nearly independent of I_2 concentration and temperature, and is inhibited by oxygen, which presumably competes with the I_2 for hydrocarbon radicals. The fact that 0.6 mole of I_2 is absorbed per mole of H_2 formed indicates that free radical production is a major component of the overall process for which the decomposition yield is about 10 bonds broken per 100 ev absorbed. Quantitative evidence as to the effectiveness of

oxygen as a scavenger for thermal organic radicals, in competition with I_2, has been obtained (78) by determining the rates of I_2 production in the γ-ray-induced radiolysis of C_2H_5I at different concentrations of O_2 and of I_2. In the absence of oxygen, I_2 production takes place only by a hot reaction and is independent of I_2 concentration. All of the thermal radicals produced by steps of the type $RI \rightarrow R+I$ return iodine to organic combination by reactions of the type $R+I_2 \rightarrow RI+I$, even at very low I_2 concentrations. When dissolved O_2 is present, the rate of I_2 production is higher as a result of competition of the reaction $R+O_2 \xrightarrow{k_1} (RO_2)$ with $R+I_2 \xrightarrow{k_2} RI+I$. The rate varies with the $[I_2]/[O_2]$ ratio in such a way as to indicate that the rate constants k_1 and k_2 are about equal.

γ-irradiation of pure degassed CCl_3Br (79) produces Br_2 at a rate which varies from 0.24 atoms per 100 ev in the solid below $-121°C.$ to about 10 at 100°. The rate is greatly increased by dissolved O_2. Contributions from a temperature independent process plus two or more slightly temperature dependent, diffusion controlled processes are suggested by the results.

Ten liquid, air-free alcohols produce reduced products (H_2 and hydrocarbons) with a combined yield of 7 to 8 equivalents per 100 ev when irradiated with 28 Mev He^{++} ions (McDonell & Newton (158)]. The oxidized products from primary alcohols are aldehydes and glycols; secondary alcohols yield aldehydes, ketones and glycols; and tertiary alcohols give primarily ketones. CO and H_2O are formed in all cases.

Polymers.—During the year under review Charlesby (159) has summarized the qualitative and some quantitative effects of ionizing radiation on long chain polymers, observed in his laboratory and elsewhere, and has speculated briefly on potential research and commercial (160) applications. Crosslinking is the predominant effect in some polymers and degradation in others. Probably the most extensive scientific investigation of radiation effects on a single polymer is that of Dole, Keeling & Rose (161) on polyethylene films exposed to pile radiation. Films were irradiated both in air and in vacuum. The effects of irradiation on infrared absorption, bromine absorption, gel formation, viscosity, and stress strain measurements were determined, and mass spectrometric analyses of the evolved gases were made. The authors report that the ratio of crosslinking reactions to those producing unsaturation is about 1 to 3, that vinylene unsaturation appears at a rate faster than vinylidene unsaturation disappears. They suggest that free radical centers may move along or across chains, through the migration of H atoms attached to the chain, until improved proximity makes possible reactions with a vinylidene group, Other investigations of polyethylene include determinations of the gases liberated during high voltage electron irradiation [Lawton, Zemany & Balwit (162)]; the effect of initial molecular weight and electron radiation dose on the extent of crosslinking [Lawton, Balwit & Bueche (163)]; and chain fission following 4 Mev electron bombardment [Baskett 164)]. Polytetrafluorethylene exposed to pile radiation shows

no crosslinking (159, 165) but decomposes yielding CF_4 as one product. Perfluoromonomers are reported to give an extremely slow rate of polymerization and low molecular weight products (166). Polymethylmethacrylate subjected to γ-rays is degraded by rupture of C—C bonds of the chain and rearrangement, added substances serving to reduce the rate of degradation [Charlesby & Ross (167)]. Charlesby has also reported during 1954 on the crosslinking of polydimethylsiloxanes (168), and the crosslinking and degradation of paraffin chains (169). He has discussed the degradation of polymers in relation to their constitution and modes of energy transfer (170); the molecular weight distribution as a function of time for polymers undergoing random fracture of the main chain (171); and the relation between radiation dose and intrinsic viscosity (172).

The rate of free radical polymerization of solutions of styrene and of methyl methacrylate in common organic solvents when exposed to a point source of β-particles has been shown to vary widely with the solvent, ranging from 0.2 radical chain starters per 100 ev for styrene to 10.2/100 ev for CCl_4 [Seitzer & Tobolsky (173)]. Possibly related to this observation is that of Ballantine (166) that emulsions of styrene show faster γ-ray-induced polymerization than the bulk material. The γ-ray-induced polymerizations of styrene and of methylmethacrylate show activation energies for the combined propagation and termination rates which agree well with values established by other means for free radical polymerization with bimolecular termination [Ballantine *et al.* (174)]. Rates of polymerization of styrene as a function of γ-ray intensity have been reported by Chapiro & Wahl (175). The γ-ray-induced polymerization of C_2H_2, both pure and mixed with other compounds, has been discussed by Lewis, Martin & Anderson (176). Other workers (177) report that the γ-ray-induced polymerization of C_2H_4 occurs at a rate which is independent of temperature from 80° to 250°C. and with an apparent activation energy of 11.3 kcal./mole above 250°, whereas, the purely thermal polymerization has an activation energy of 50 kcal./mole and is negligible in rate below 450°.

Dosimetry.—Until recently there has been a serious uncertainty as to the absolute yield of the very useful ferrous sulfate dosimeter. Different workers reported from 15.6 to 21 Fe^{++} ions oxidized per 100 ev of high energy β- or γ-radiation absorbed, and there was no obvious reason for the discrepancy. Three investigations reported during 1954, together with their analysis of previous work, seem to make it safe to conclude that the true yield is within a few per cent of 15.7. Saldick & Allen (178) have obtained $G = 15.6 \pm 0.5$ by delivering to a solution a measured charge of 1 Mev or 2 Mev cathode rays; Lazo, Dewhurst & Burton (179) have obtained 15.8 ± 0.3 by a calorimetric method; and Weiss, Bernstein & Kuper (180) have obtained 15.9 ± 0.5 by application of the Bragg-Gray principle to ionization chamber measurements.

Hart & Walsh (63) have shown that the addition of Cu^{++} to the ferrous sulfate dosimeter reduces $G_{Fe^{++}}$ for γ-rays from 15.6 to 0.66 but that the corresponding reduction for recoils from the $B^{10}(n,\gamma)Li^7$ reaction is only

from 4.2 to 2.0. Consequently when Fe^{++} dosimeter solutions containing Cu^{++} with and without boric acid are exposed to radiation containing both γ-rays and thermal neutrons, the separate γ- and neutron intensities can be deduced from the amounts of Fe^{++} oxidized. Likewise, if Fe^{++} dosimeter solutions containing 1 m*M*. KI are exposed with and without added boric acid the absolute and relative rates of gas evolution from the two solutions may be used to deduce the value of both the γ- and neutron fluxes in high flux pile radiation [Hart & Gordon (181)].

Silver-activated glass, which has been produced in commercial quantities has been shown by Schulman, Klick & Rabin (182) to undergo a nearly linear increase in optical density with irradiation which makes it useful for measuring doses in the range of about 10^3 to 10^6 rep.

Discussions of principles and practical problems involved in absolute dose determinations, in addition to those in references cited above, are given by Fano (183, 184) and by Cormack & Johns (185).

Irradiation sources.—In addition to the designs of research irradiation chambers using Co^{60} reported in the last review of this series (11) new designs were described in 1954 by Schwarz & Allen (186) and by Eastwood (187). The preparation of a kilocurie fission product source was described by Loeding *et al.* (188), and, in connection with this work, Dillon, Burris & Rodger (189, 190) have outlined methods for calculating the radiation intensity at the center of a radioactive hollow cylinder.

Industrial applications.—Nucleonics (191) has tabulated information about 40 organizations which are working on problems related to the use of radiation in processing foods and drugs. A preliminary survey of the effects of pile irradiation on the mechanical and physical properties of a number of structural engineering materials, with references, is given by Leeser (192).

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THE QUANTUM THEORY OF VALENCE[1]

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This review will cover what may for short be termed "valence theory": theory of electronic structure of molecules in normal states, in excited states, and in course of reaction.

In 1954, the Nobel Prize in Chemistry was awarded to Linus Pauling, partly in recognition of his work on the nature of the chemical bond (1). Elucidation of the nature of the chemical bond must remain the first purpose of research in valence theory, but the emphasis in recent years, and in 1954, has been elsewhere. Receiving more attention have been two other branches of valence theory, the semi-quantitative theory of unsaturated organic molecules and the quantitative theory of atoms and simple molecules. These will be the subjects of the first and second parts of this review. Also discussed in the second part will be dissociation energies of simple molecules, directed valence, and hybridization.

In the way of basic theory, the most important work of 1954 concerns the atomic valence state and the valence bond method; these will be considered in the third part of the review. In the final part, certain additional contributions of the year will be cited, and certain trends that are apparent will be noted.

Unsaturated Organic Molecules

The changing theory.—Research on the theory of the electronic structure of unsaturated organic molecules may be characterized as a continuing search for a best compromise model for treating many properties of many molecules, a model simple enough to be manageable, yet detailed enough to be useful. In recent years there has been much activity in this search, producing radical changes in theory still in process in 1954. This should be borne in mind in any consideration of the year's work.

For any molecule, the central problem of valence theory is to find, for fixed nuclear configurations, mutually orthogonal electronic wave functions ψ_{el} which make the expectation value for the electronic energy,

$$E_{el} = \int \psi_{el} H_{el} \psi_{el} d\tau \Big/ \int \psi_{el} \psi_{el} d\tau, \qquad 1.$$

a minimum, where H_{el} is the Hamiltonian operator defining the electronic motions for the molecule in question (2). The various functions ψ_{el} describe the normal and excited electronic states of the molecule, and from them any desired molecular property may be computed. Generally the computation of

[1] The survey of the literature pertaining to this review was concluded in January, 1955.

a property from the ψ_{el} is a problem of lower order of difficulty than is the determination of the ψ_{el} themselves.

One ordinarily does not examine all possible functions to see whether they minimize the expression 1. Instead, one considers functions of some restricted class, and one selects that function which gives the lowest energy. This "variational method" is fundamental in valence theory.

In principle, difficulty rarely is met in writing down a correct electronic Hamiltonian H_{el}, since rules for doing this for systems made up of electrons and nuclei are well-known (3). If relativistic and magnetic effects are neglected, H_{el} for a molecule in isolation simply contains terms representing the kinetic energy and the coulombic potential energy of the electrons. For atoms and simple molecules, one does indeed write out H_{el} in this way, and one then proceeds to the determination of the ψ_{el}. The problem is thus reduced to a purely mathematical one—to improve trial functions by addition of more and more variational parameters.

For complex unsaturated molecules, the problem could be attacked in the same way, but in practice it is not. In place of writing out the complete many-electron Hamiltonian operator, one explicitly considers only the so-called π-electrons (two electrons in ethylene, six in benzene, and so on). The other electrons, the σ, merely are treated as supplementing the nuclear field in which the π-electrons move. One writes

$$H_{el}^{\pi} = \Sigma_i H_{\text{core}}(i) + \Sigma_{ij}(e^2/r_{ij}), \qquad 2.$$

where $H_{\text{core}}(i)$ includes the kinetic energy of π-electron i, its potential energy of attraction for all nuclei, and its potential energy of coulomb repulsion and exchange attraction for σ-electrons; the electronic repulsion terms (e^2/r_{ij}) pertain to π-electrons only. One then turns to the determination of the π-electron wave functions by application of the variational method. This procedure represents what is known as the "π-electron approximation."

As has been emphasized by McWeeny (4), equation 2 may be derived from the correct Hamiltonian operator on the sole assumption that the σ-electrons occupy in pairs a set of framework orbitals that are independent of the π-electronic state. A simpler form of π-electron Hamiltonian also is in use, namely,

$$H_{el}^{\pi} = \Sigma_i H_{\text{effective}}(i). \qquad 3.$$

This, however, is much more approximate; π-electron repulsions have been suppressed in a manner that cannot be justified theoretically.

In the simple molecular orbital method of Hückel (5), as extended and applied to a host of chemical problems by Coulson & Longuet-Higgins (6), equation 3 is used. For a molecule having n π-electrons, it follows that the variational problem reduces to n identical one-electron problems and that the total wave functions ψ_{el}^{π} are expressible in terms of products of one-electron molecular orbitals ϕ_i. A typical "ground state" wave function, for example, has the form

$$\psi_{el}^{\pi} = \phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\cdots. \qquad 4.$$

"Excited state" functions similarly may be constructed by assignment of electrons to higher-energy molecular orbitals, no more than two electrons in an orbital. In certain cases, linear combinations of such product functions may give better representations of actual molecular states than single products (7). But electron spin is not explicitly brought into the wave function.

In the Hückel method the molecular orbitals (MO) are approximated as linear combinations of atomic orbitals (LCAO):

$$\phi_i = \Sigma_p C_{ip} \chi_p. \qquad 5.$$

Here χ_p denotes a $2p\pi$ atomic orbital (AO) on atom p; the C_{ip} are numerical coefficients. The "best" ϕ_i, or "best" C_{ip}, are found by minimizing with respect to the C_{ip} an energy integral like equation 1, with ϕ_i replacing ψ_{el} and $H_{\text{effective}}$ replacing H_{el}. This brings in integrals of three types, overlap integrals between atomic orbitals,

$$S_{pq} = \int \chi_p(1)\chi_q(1)dv(1), \qquad 6.$$

coulomb integrals for atoms,

$$\alpha_p(\text{eff}) = \int \chi_p(1)H_{\text{effective}}(1)\chi_p(1)dv(1), \qquad 7.$$

and resonance integrals for bonds,

$$\beta_{pq}(\text{eff}) = \int \chi_p(1)H_{\text{effective}}(1)\chi_q(1)dv(1). \qquad 8.$$

In the Hückel scheme, overlap integrals are computed theoretically or neglected, coulomb integrals are taken to be empirical properties of atoms, and resonance integrals are taken to be empirical properties of bonds (zero for non-bonded atom pairs). For many important molecular properties, coulomb integrals cancel or nearly cancel out of the formulas, and overlap effects are small. The relatively recent series of papers by Dewar (8) and Dewar & Pettit (9) involve essentially an extension of the Hückel technique.

The chief practical disadvantage of the simple Hückel method is that it does not give a satisfactory account of spectroscopic properties. In benzene, for example, the two excited states experimentally observed at 3.8 and 6.2 ev would according to the Hückel theory be degenerate, each with the energy -2β, where β is the resonance integral for an aromatic carbon-carbon bond. Furthermore, the value of β required to fit the vertical resonance energy of benzene is -1.7 ev.

The method of Goeppert-Mayer & Sklar (10) leads to a better explanation of the spectra of unsaturated molecules. In this method one uses equation 2 for the Hamiltonian operator. In order to take proper cognizance of the Pauli exclusion principle, one employs antisymmetrized determinantal wave functions such as

$$\psi_{el}^{\pi} = (n!)^{-1/2} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \phi_2(1)\alpha(1) \cdots \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \phi_2(2)\alpha(2) \cdots \\ \cdots & \cdots & \cdots \quad \cdots \end{vmatrix} \qquad 9.$$

or linear combinations of such functions, where α and β are spin functions. Techniques for working with determinantal functions were worked out in the early days of wave mechanics; standard rules are available for computation of an energy integral like equation 1 (11).

The molecular orbitals ϕ_i again are approximated as linear combinations of atomic orbitals. The integrals that enter in the denominator of equation 1 then can be reduced to the overlap integrals of equation 6; in the numerator there will enter coulomb and resonance integrals involving H_{core} instead of $H_{\text{effective}}$,

$$\alpha_p(\text{core}) = \int \chi_p(1) H_{\text{core}}(1) \chi_p(1) dv(1)$$

and

$$\beta_{pq}(\text{core}) = \int \chi_p(1) H_{\text{core}}(1) \chi_q(1) dv(1), \qquad 10.$$

and, from the e^2/r_{12} terms in the Hamiltonian, a new type of integral, electronic repulsion integrals,

$$(pq|rs) = \int \chi_p(1)\chi_q(1)(e^2/r_{12})\chi_r(2)\chi_s(2) dv(1) dv(2). \qquad 11.$$

For a large unsymmetrical molecule in which N atomic orbitals are available for accommodation of π-electrons, there enter $N^4/8$ distinct integrals of this last type.

In the Goeppert-Mayer-Sklar method all integrals are calculated by theoretical means utilizing Slater $2p\pi$ AO's; reasonable approximations are invoked to elucidate H_{core}.

The original Goeppert-Mayer-Sklar calculation of the benzene spectrum (10) has been redone twice, first to correct an error in one of the electronic repulsion integrals (12, 13, 14), and then to include a number of integrals that originally had been neglected (15). The effect of variation of the effective charge in the carbon atomic orbital has also been examined (16).

Two contributions have been important in the later development of the Goeppert-Mayer-Sklar method. Roothaan (17) provided the machinery required for the systematic "self-consistent field" calculation of the best C_{ip} in cases where these are not determined completely by symmetry [e.g., butadiene (18)], and Craig (14) demonstrated that it was feasible to mix many more single determinants in approximating molecular states than were considered by Goeppert-Mayer and Sklar. This "configuration interaction" has been exhaustively studied in benzene (19); the final results for the energy levels are in fair agreement with experiment.

A final refinement of the benzene calculation has been provided recently by Niira (20), who computed corrections for σ-π exchange. The elucidation of H_{core} given by Goeppert-Mayer & Sklar and followed by others had neglected σ-π exchange terms. The theoretical considerations of McWeeny (4) or the equations of Roothaan (17) show that inclusion of σ-π exchange effects in H_{core} is possible; Niira has now accomplished this for benzene. The effects of exchange are neither large nor negligible.

The disadvantages of the Goeppert-Mayer-Sklar method are two. First, there is the "N^4 difficulty" implied above—the electronic repulsion integrals met in benzene can be handled, but 32,131 of these occur in 1-methylpentacene! Secondly, the very "purely theoretical" nature of the treatment detracts from its present value as a tool for prediction—as it now stands the method fails to give really good agreement with experiment, and there is no way provided for calibrating the method with known data.

Modifications in the Goeppert-Mayer-Sklar method were initiated by Moffitt in two important papers. In the first (21) he considered the oxygen molecule, a simple prototype of unsaturated organic molecules for which many good spectroscopic data are available. He applied the standard Goeppert-Mayer-Sklar method and found results which were disappointing. He then identified a principal difficulty: the unmodified Goeppert-Mayer-Sklar method improperly places the various states of the atoms, O^+, O ,O^-, on the energy scale relative to one another. The reasons for this were discussed at length by Moffitt and will not be gone into here; suffice it to say that he proceeded to find a way to correct for the error: he referred molecular energy levels to actual (as opposed to calculated) energy levels of atoms in isolation. Combined with empirical adjustment of one resonance integral, this gives very good agreement with experiment for oxygen. In the second paper (22), Moffitt gave an elaborate prescription for a general method of "atoms in molecules."

Later work seems to have established that whatever merit the atoms-in-molecules idea has for accurate calculations, it has considerable merit for calculations within the π-electron approximation. In studies of ethylene, allyl radical, cyclobutadiene, and benzene, Moffitt & Scanlan (23, 24, 25) have obtained considerable improvement over Goeppert-Mayer-Sklar results. For example, the Goeppert-Mayer-Sklar calculation on ethylene (26) gives much too high an energy separation between the first singlet and first triplet excited states; this is put right by an atoms-in-molecules correction (24). For such hydrocarbon systems, this correction may be viewed as the replacement of the computed (16.93 ev) energy change for the process, $C+C \rightarrow C^+ + C^-$ (all atoms), by an empirical value (11.08 ev); atoms-in-molecules correction gives carbon-carbon double bonds more ionic character than does the unmodified Goeppert-Mayer-Sklar method.

That approach which has been termed the generalized Hückel method may now be described. This has been developing recently both in England (27, 28, 29) and in America (30 to 33). In the English work, the emphasis has been on Roothaan's self-consistent field procedure and properties of molecules in normal states; in the American work, the emphasis has been on Craig's configuration interaction procedure and electronic spectra. But there is no fundamental difference.

In the generalized Hückel method one uses the Goeppert-Mayer-Sklar theoretical framework. However, one applies atoms-in-molecules corrections, one neglects all overlap integrals $S_{pq}(p \neq q)$, one treats α(core)'s and β

(core)'s empirically much as the α(eff)'s and β(eff)'s are treated in the simple Hückel method, and one sets equal to zero all electronic repulsion integrals $(pq|rs)$ save those $N(N+1)/2$ of the form $(pp|qq)$.

The assumption that reduces the electronic repulsion problem to the evaluation of the $(pp|qq)$ integrals, that of "zero differential overlap" (34), has the effect of making application of atoms-in-molecules corrections very easy, at least for hydrocarbons; one simply sets $(pp|pp)$, the one-center electronic repulsion integral, equal to $I_p - A_p$, where I_p and A_p are the appropriate atomic ionization potential and electron affinity (35). Thus for $tr^3\pi$-carbon, one takes the value $11.54 - 0.46 = 11.08$ ev for this integral, instead of the theoretically computed 16.93 ev.

How the repulsion integrals $(pp|qq)$ should be determined in this method is a crucial question that remains open. In calculating the spectra of polyacenes, Pariser (33) has used values of these integrals which fit the benzene spectrum exactly; these values fall a little below theoretical values computed for Slater orbitals with effective charge 3.18. Pople first (27) took the simple approximation $(pp|qq) = e^2/R$, where R is the distance between atoms p and q; he has since (28) turned to the values prescribed by Pariser.

Practical applications of the generalized Hückel method were first made to the electronic spectra of ethylene, butadiene, benzene, and the nitrogen heterocyclic analogues of benzene (31). Both energies of excitation and transition probabilities came out well. Then, Pople (27) showed that resonance energies and ionization potentials of a number of simple hydrocarbons could be explained by the method. The long-standing discrepancy between naphthalene bond lengths theoretically predicted and experimentally found was also resolved (27, 29, 33).

Recent work with the generalized Hückel method has continued to yield encouraging results. Brickstock & Pople (28) have given a detailed discussion of resonance energies and charge distributions of hydrocarbon ions and radicals. They have demonstrated that the resonance energy of a conjugated ion, either positive or negative, is greater than that of the corresponding radical and that in conjugated ions there is a tendency for the electrons to keep to the central parts of the molecule. Pariser (33) has calculated the spectra of the polyacenes from benzene through pentacene, providing confirmation for a number of spectroscopic assignments and making predictions of many new singlet and triplet states. And finally, detailed treatments of the butadiene molecule by Pullman & Berthod (36) and Moser (37) have given satisfactory results for both transition probabilities and location of energy levels.

Concerning the assumptions peculiar to the generalized Hückel method, it had been suggested (32) that the zero differential overlap scheme can be viewed as an approximation to a more exact calculation using the orthogonalized atomic orbitals of Löwdin (38). This conclusion has now been substantiated by McWeeny (39) in valence-bond calculations on the benzene molecule. Hall (40) has come to a similar conclusion through calculations on butadiene using localized orthogonal orbitals derived from his standard-

excited-state method. As for empirical treatment of core integrals, McWeeny (4) also has provided justification here: empirical α's and β's may be regarded both as including σ-π exchange effects and as transcending the assumptions inevitably required for their purely theoretical calculation (e.g., use of hydrogen-like AO's).

The encouraging results obtained through the admittedly semiempirical generalized Hückel method have motivated the search for purely theoretical improvements of the usual Goeppert-Mayer-Sklar approach. Thus Sponer & Löwdin (41) have investigated whether use of Hartree-Fock atomic orbitals in place of Slater orbitals would help; apparently it does not. On the other hand, Ohno & Itoh (42) have obtained good results for ethylene and oxygen employing two Slater $2p\pi$ orbitals on each atom, one with an effective charge appropriate for the neutral atom, the other with an effective charge appropriate for the negative ion.

Choice of β(core)'s as empirical parameters in the generalized Hückel method is tantamount to assuming that these quantities can be carried over from one molecule to another. Goodman & Shull (43) have recently proposed a theory which involves a slightly different choice of molecular invariants.

The theory, then, is changing. It seems rather definite, however, that a trustworthy method of one form or another will soon be available for correlation and prediction of the diverse properties of alternant hydrocarbons. The corresponding theory of heteromolecules is not so far along. Here much effort will doubtless be expended in the next few years—at the very least, detailed understanding of certain types of molecular perturbations should emerge; at the very best, useful schemes for treating many properties of many molecules may evolve.

Applications of theory to spectra and other properties.—A number of applications of the newly developing generalized Hückel method have already been referred to (27 to 33, 36, 37); applications of older methods naturally have been much more widespread. Thus the simple Hückel method has been employed by Perez, Herráez & Igea (44) in calculations of charge densities, bond orders, free valences, and localization energies for aniline, methylaniline, dimethylaniline, diphenylamine, and triphenylamine; by Alonso & Peradejordi (45) in calculations of some of these quantities for biphenylene; by Simonetta & Vaciago (46) in calculations of some of them for nitrobenzene; and by Paoloni (47) in calculations of some of them for substituted *p*-benzoquinones. Masse has used the method both in considering the spectroscopic effects of methyl substitution in pyrene (48) and in rationalizing the chemical behavior of spiran-type molecules in the presence of light (49); and Brown & Dewar (50) have used it in treating the spectra of fluorene analogues of triphenylmethane dyes.

The Goeppert-Mayer-Sklar method, with emphasis on Roothaan's self-consistent field (SCF) procedure or Craig's configuration interaction (CI) procedure, has been employed by Pullman (51) in CI calculations of electronic energy levels and transition probabilities in butadiene, by Shida

(52) in SCF calculations of electronic energy levels in cyclobutadiene, by Serre (53) in SCF calculations of wave functions and energy levels in diacetylene, by Bassompierre (54) in SCF calculations of wave functions and energy levels in hydrogen cyanide, and by Julg (55) in SCF calculations on the azulene molecule. In the last-mentioned study, the dipole moment of the molecule was computed and found to agree with the observed (presumed mainly π) moment; an earlier SCF calculation by Berthier (56) of the dipole moment of fulvene had also given a good result. Perhaps the most interesting SCF calculation on an unsaturated molecule to date is the calculation by Fischer (57) of the dipole moment of aniline; this professional work clearly shows the nature of the problems met in any such calculation on a large molecule containing heteroatoms. Finally, one should note the SCF calculation by Berthier (58) of transition probabilities in ethylene, butadiene, and fulvene, and the CI calculation by Itoh, Ohno & Yoshizumi (59) of the diamagnetic anisotropy of benzene.

The new valence-bond method of Simpson (60) for handling π-electron spectra has now been further elaborated by Simpson & Looney (61) and applied by them to the color of triphenylmethane dyes (62). This method involves extracting information about generalized "contributing resonance structures" from molecular spectra in much the way that information about the equivalent orbitals of Lennard-Jones (63) can be obtained from molecular ionization potentials (64). The procedures suggested would appear to have most value for molecules possessing high symmetry.

Several recent papers (65 to 70) have been concerned with the basic definitions of or techniques for computing bond orders, resonance energies, and localization energies in conjugated molecules. A number of papers dealing with molecular polarizability have also appeared (71 to 74).

Recently there has been a great deal of interest shown in the spectra of the polyacenes, the molecules benzene, naphthalene, anthracene, etc. (7, 33, 75, 76, 77); three closely-related treatments of these spectra have been given. The work of Moffitt (76) is intermediate with respect to simplicity and degree of empiricism. Viewing each molecule as a perturbation of a corresponding circular molecule having the same number of carbon atoms (perimeter model), he has semiquantitatively explained the observed behavior of the four low-lying singlet excited states as the number of rings increases (including a crossing of the two lowest levels). He chooses separately an empirical Hückel β(eff) for each state from the known benzene spectrum, determines energies of excitation by applying the simple Hückel method to the reference circular molecules, and then corrects for perturbing effects of crosslinks by use of one more empirical parameter. He further explains a number of spectroscopic effects in other cata-condensed hydrocarbons and briefly discusses the influence of substituents.

According to the Hückel theory, in any alternant hydrocarbon a degeneracy is present between two of the four low-lying excited electronic states. Dewar & Longuet-Higgins (7) take this fact as the starting point for their

theory of polyacene spectra. Invoking the "first-order" configuration interaction between these two degenerate states, they too have explained the main features of these spectra, thus removing the need to consider pentacene, for example, as a perturbation of a molecule having 22 carbon atoms in a ring. Moffitt (77), nevertheless, still argues that the perimeter model is best.

The treatment by Pariser (33) is aimed at more completeness. Using the generalized Hückel method and no empirical data except molecular dimensions and the spectrum of benzene, he has computed the low-lying singlet and triplet electronic energy levels of the polyacenes through pentacene. Agreement with experiment is striking; theory versus experiment in the case of naphthalene has been discussed in detail by McClure (78). Pariser has also noted the chemically interesting result that for any alternant hydrocarbon there exists a degeneracy between a certain singlet excited state and the corresponding triplet.

As theory progresses, more and more properties should begin to fall into a single coherent theoretical scheme (one set of theoretical assumptions or one set of values for empirical parameters or both). Current literature shows how ripe the situation is for development in this direction. Thus Bergman (79) has discussed relations between half-wave potentials and absorption spectra for aromatic hydrocarbons; Nagakura & Kuboyama (80) have considered dipole moments and absorption spectra of *o*-benzoquinone and related substances; Sponer (81) has discussed wavelength shifts in spectra of fluorinated benzenes in terms of inductive and mesomeric effects of the fluorine atom; and Goodman & Shull (82) have begun theoretical studies relating the so-called n-π absorption spectra of molecules to their ionization potentials. All of these properties, and more, would come together under a useful theory.

Chemical reactivity.—Fukui *et al.* (83, 84, 85) have developed further what they call the frontier electron theory of reactivity in conjugated molecules (86). Successful applications have now been made to electrophilic, radical, and nucleophilic reactions in various aromatic and other conjugated molecules (83, 84), and a simple and neat justification for the theory has been given (85).

This theory starts from the reasonable idea that the less tightly bound electrons in a molecule should have greater influence upon reactivity than the more tightly bound. Frontier electrons must be specified appropriately according to the type of reaction, but the electron densities of these frontier electrons are then found to correlate better with points of attack than do total electron densities. For example, according to either the simple or the generalized Hückel theory, total π-electron densities are the same on all carbon atoms in alternant hydrocarbons (27, 87); on the other hand, electron densities for the highest filled molecular orbitals are not uniform and, in fact, are high at points of preferential electrophilic attack (86).

In justification of the frontier electron theory, Fukui *et al.* (85), following Muller, Pickett & Mulliken (88), adopted as a model for the transition state

in a substitution reaction a structure in which the aromatic π-orbitals are conjugated with a pseudo-π-orbital made from the two orbitals on displacing atom and atom being displaced (one above the ring, one below). They then showed that the main part of the stabilization of transition state brought about by this conjugation is attributable to the frontier electron density near the reaction center.

Through study of ionization potentials and electronic excitation energies for various nucleophilic and electrophilic groups (the difference between two molecular ionization potentials is not in general equal to an electronic excitation energy), Nagakura & Tanaka (89) have presented support for an electrophilic aromatic substitution mechanism the first step of which is the transfer of a π-electron from the aromatic molecule to a low-lying orbital of the substituent. They also have averred that the electron-attracting (meta-orienting) groups in substituted benzenes are those which have low-lying vacant orbitals (90).

Green (91) has given some applications of valence-bond theory to aromatic substitution. Theoretical studies have continued on Hammett's equation and inductive and mesomeric effects of various substituents in aromatic molecules (92 to 95). A review of the attempts to relate carcinogenic activity of aromatic hydrocarbons to their electronic structure has been given by A. Pullman (96), more general reviews of electronic structure and chemical reactivity by B. Pullman (97) and by Chalvet (98).

The free-electron model.—Developments and applications of free-electron models of conjugated systems have continued (99 to 112). In the most common form of this model, the free-electron network model, the π-electrons are assumed to move with complete freedom along or around the conventional bond structure for a molecule—up and down a polyene chain, or round and round a benzene ring.

That the free-electron network model deserves equal footing with and is in a sense equivalent to the simple LCAO molecular orbital method of Hückel, at least for alternant hydrocarbons, first claimed by Simpson (113), has now been demonstrated in detail by Ruedenberg (99) and Griffith (100). Introduction of heteroatoms has not yet been effectively accomplished in the free-electron model, although attempts have been made (101, 102).

The inclusion of electronic repulsion in the free-electron model is very difficult. While the molecular orbital treatment of this is well-advanced, in the free-electron network model all electronic repulsion energies turn out to be infinite if the electrons are assumed to move along strictly one-dimensional paths. Some device must be introduced to get rid of these infinities, which invariably brings in new parameters. Thus for polyenes, Araki & Araki (103) have assumed that the one-dimensional potential corresponding to e^2/r_{12} may be taken as the transversal average of e^2/r_{12} over a parallelepiped of cross-sectional area A; for catacondensed hydrocarbons, Araki & Murai (104) have assumed that e^2/r_{12} may be set equal to zero for r_{12} less than a certain cutoff radius r_0.

More analogous to the older free-electron theory of metals is the box model for conjugated systems, first proposed by Schmidt (114). Platt (105) has now established an amazing result: ten electrons free to move in a rectangular box give the total π-electron density surface closely reproducing the geometry of the bond skeleton of the naphthalene molecule!

Successful handling of the mathematics of the free-electron network model of conjugated molecules hinges on the fact that the wave-functions on the separate rings and chains may be considered one-dimensionally if they are properly fitted together at branch points (e.g., the 9 and 10 positions in naphthalene). One boundary condition at a branch point is that the wave function be continuous. Another condition usually is taken to be that the incoming derivatives add up to zero (115), but the necessity of this has recently been questioned by Kuhn (106).

Atoms and Simple Molecules

Variational calculations of atomic wave functions.—Electronic wave functions for atoms are of interest to a physical chemist both for their own sake [e.g., for calculations of atomic scattering factors for use in x-ray crystal structure analysis (116)] and because, after all, an atom is but a simple molecule; wave mechanical techniques designed for calculations on molecules may first be tested on atoms. It should be noted, however, that the energy changes of interest in physical chemistry are of the order of the energies of excitation in atomic spectra, much less than the total energies of atoms referred to separated electrons and nuclei (22); the problems of valence theory are of the same level of difficulty as are the problems of atomic spectra.

In the traditional method for obtaining wave functions for atoms, the Hartree-Fock method (117), one seeks the best possible one-electron atomic orbitals for use in single-determinant wave functions like equation 9. These orbitals are not assumed to have simple analytical form; rather, each is regarded as defined by a table of values of a radial part $f(r)$ of a function $f(r)$ $S(\theta, \phi)$, where $S(\theta, \phi)$ is an appropriate surface harmonic. The best functions $f(r)$ are found using numerical variational methods. Recent calculations using this method include those by Morrow (118) on Cu^+ and by Henry (119) on Au^+. A study of more general interest has been made by Löwdin (120), who has treated in detail a quantity Z' for a Hartree-Fock orbital analogous to the effective nuclear charge Z in a hydrogen-like orbital. For consecutive atoms or ions, Z' is linear with atomic number and so is useful for interpolation.

From the molecular standpoint, Hartree-Fock-type calculations have two disadvantages: first, the practical techniques are laborious and completely unsuitable for extension to molecular problems; and, secondly, although absolute energies of the various electronic states are determined to an accuracy of about 0.5 per cent, this is not enough to give quantitative assessment of excitation energies.

The first difficulty can be resolved by use of analytical one-electron functions containing parameters varied to minimize the energy. The Coulson-Duncanson orbitals (121) are of this type; the errors in total energy do not exceed one per cent for atoms of the first short period. More recently, Green *et al.* (122) have studied improved analytical one-electron orbitals for the $1s$ electron in the $1s^2$ ground states of the atoms H^- through C^{+4}.

The inaccuracy of single-determinant wave functions (whether built from Hartree-Fock or analytical atomic orbitals) stems from the fact that they do not properly account for the correlation of electronic motions. Two procedures are available for obtaining more accurate functions. In the first, the interelectronic distances r_{ij} are introduced explicitly into trial variation functions. Hylleraas (123) used this method for the ground state of the helium atom and obtained precise agreement with experiment. But such calculations are tedious, they destroy the useful orbital description, and they are impractical for systems containing more than two electrons.

The second and unquestionably the best procedure for securing wave functions of any desired accuracy is the method of superposition or interaction of configurations. Single determinants like equation 9 can be combined linearly to give improved wave functions *ad infinitum;* the exact wave function can be approached by combination of more and more such determinants provided the one-electron functions employed form a complete set. Such a procedure at first sight seems very different from explicit introduction of the r_{ij} into the wave function. The two methods are equivalent, however; the relation between them has been examined by Green *et al.* (124, 125) for a few two-electron cases in which good wave functions involving r_{12} can be obtained.

Very significant calculations of atomic wave functions have been performed by Boys (126 to 131), who uses analytical one-electron orbitals and the method of configuration interaction. His calculation, with Price (130), of wave functions and energies of two states of Cl, one state of Cl^-, three states of S, and two states of S^-, even including relativistic corrections, appears to be a brilliant technical achievement. Previously, he had considered, with comparable accuracy, three states of Be and B (128, 129), one state of F^-, Ne, and Na^+ (127), and five states of C (129), in the last case determining energies of ^3P, ^1D, ^1S, ^5S, and ^3D states with an average error in energy of 0.25 per cent (computed ^5S-^3P separation 3.8 ev, experimental 4.2 ev).

Molecular wave functions and dissociation energies.—The determination of molecular wave functions is harder than the determination of atomic wave functions because the potential energy of nucleus-electron attractions involves two or more nuclear centers instead of one. This simple fact creates a barrier of the first magnitude: the integrals that enter the variational calculations are much more difficult to calculate for molecules than for atoms. Work on these integrals is of vital importance and has continued (132 to 138).

Variational calculations recently have been reported for H_2^+ (139 to

143), H_2 (143 to 146), Li_2 (147), CH (148), NH_2 (149), NH_3 (150), HF (151, 152), LiF (153), N_2 (154, 155), O_2 (42, 156), and F_2 (157).

Very accurate wave functions already are available for H_2^+ and H_2. In the first case, precise numerical determination of molecular orbitals and energies for various states is possible (158); in the second, the method used by Hylleraas on the helium atom may be applied (159). Neither of these methods can be practicably extended to other molecules, although Wallis & Hulburt (144) have succeeded in performing a calculation on H_2 using numerical H_2^+-like wave functions. One needs a different method; as in atoms, the most promising approach is by configuration interaction using some set of starting one-electron wave functions.

The H_2^+ and H_2 molecules are of quantum-mechanical interest, then, as simple molecules on which new methods may be tried. Unique calculations on H_2^+ have been made by Streetman & Matsen (139), by Hurley (143), and by Dalgarno & Poots (140). Streetman & Matsen approximate the ground state by a linear combination of two 1*s* hydrogen-like atomic orbitals on the two nuclei, effective charge Z, and a third hydrogen-like orbital centered between the nuclei, effective charge Z'. Hurley uses a linear combination of two 1*s* hydrogen-like atomic orbitals, effective charge Z, symmetrically located a distance αR apart, where R is the internuclear distance. Dalgarno & Poots use a linear combination of two 1*s* orbitals on the nuclei, effective charge Z, and a third function which is the geometric mean of another pair of 1*s* atomic orbitals on the nuclei, effective charge Z'. Varying Z and Z' subject to the condition $Z \geqq Z'$, Streetman & Matsen obtain a dissociation energy of 2.64 ev, with $Z = Z' = 1.25$; varying Z and α independently, Hurley obtains a dissociation energy of 2.67 ev, with $Z \sim 1.2$, $\alpha \sim 0.9$; varying their Z and Z' independently, Dalgarno & Poots obtain a dissociation energy of 2.79 ev, with $Z = Z' = 1.354$. These energies may be compared with the result obtained with just the two orbitals on the nuclei, 2.26 ev, the result obtained by hybridizing 1*s* and $2p_s$ orbitals on the two nuclei, 2.73 ev, and the theoretically exact result, 2.81 ev. Dalgarno-Poots-type orbitals would seem well worth further investigation.

Hurley (143) also has considered the use of "floating" atomic orbitals for H_2, which previously had been attempted by Gurnee & Magee (160). Other theoretical work on this molecule has been performed by Altmann & Cohan (145). These authors have repeated Weinbaum's early calculation (161) in which the simple Heitler-London covalent wave function is improved by the addition of ionic terms. Weinbaum demonstrated that the minimum energy occurs when $Z_c = Z_i = 1.193$, where Z_c and Z_i are effective charges for the atomic orbital in the covalent and ionic terms. Altmann & Cohan have confirmed this, and they have discussed in detail the general problem of preselection of Z values in covalent and ionic contributing structures.

Scherr (146) has shown that if one sets $Z_c = Z_i = 1.0$ in a Weinbaum-type wave function for H_2 and replaces the theoretical electron affinity of the hydrogen atom wherever it appears in the calculation by the empirical

affinity, one obtains a dissociation energy of 4.77 ev; the Weinbaum result is 4.02 ev, the exact result 4.73 ev. This is an "atoms-in-molecules" correction of the type advocated by Moffitt (22); unfortunately, the choice of Z values is crucial and hard to justify.

Atoms-in-molecules corrections have been applied in few other cases. Some applications to unsaturated molecules have already been indicated; otherwise there is only a calculation by Rahman (147) on Li_2 and one by Kastler (151) on HF. Rahman has given a simplified treatment of certain spectroscopic states of Li_2 both with and without atoms-in-molecules corrections. Kastler has treated the ground state of HF by the valence-bond method, including three covalent and three ionic structures. To systematize the calculation he employs orthogonalized atomic orbitals in a manner anticipating later proposals of McWeeny (162). Without atoms-in-molecules correction he obtains a dissociation energy of 2.0 ev and a dipole moment of 0.9 D; with atoms-in-molecules correction he gets a dissociation energy of 5.7 ev and a dipole moment of 2.7 D; the experimental energy and moment are 6.6 ev and 1.9 D. The atoms-in-molecules correction in this case amounts to a downward adjustment of the energy of the structure H^+F^- relative to H—F; it gives the H—F bond more ionic character than does the uncorrected theory.

Single-determinant wave functions like equation 9 furnish descriptions of molecules that are satisfactory for most qualitative and many quantitative purposes. Determination of the best numerical (Hartree-Fock) orbitals in such descriptions is neither practicable nor especially desirable for molecules, but a well-defined method approximating this is available: Roothaan's LCAO self-consistent field (SCF) procedure (15), in which each molecular orbital is approximated by a linear combination of atomic orbitals, as in equation 5. LCAO SCF treatments considering all electrons explicitly and taking proper account of all orthogonality requirements now are available for LiH (163), HF (152), N_2 (155), H_2O (164), and NH_3 (150). Computed (experimental) dissociation energies (ev) are as follows: LiH, 2.0 (2.5); H_2O, 7.7 (10.1); NH_3, 22.8 (25.3); for HF and N_2 computed dissociation energies also are less than the observed.

The LCAO SCF method, like the Hartree-Fock method itself, is most apropos for closed-shell ground states. Extensions of the method are required when the number of electrons is odd, as in radicals, or when a single determinant is not a good description, as for many spectroscopic excited states. The mathematical equations for radicals have been considered by Pople & Nesbet (165) and by Berthier (166), and a special procedure for excited states has been invented by Nesbet (167). Some applications to the simple radicals CH and NH_2 have been given by Higuchi (148, 149).

If sufficient configuration interaction (CI) is superposed upon a SCF treatment, the choice of LCAO coefficients becomes immaterial; a SCF treatment is less general than a complete CI treatment. Similarly, CI in-

cludes the valence-bond procedure as a special case. These relations are well-illustrated by Higuchi's work on CH (148).

A complete CI treatment will give the exact molecular wave function only if the initial one-electron base orbitals form a complete set; a CI calculation starting from a particular finite set of orbitals can give results of only limited accuracy. Often it has been said that Hartree-Fock atomic orbitals are preferable to Slater orbitals as base functions for CI calculations on molecules; this is not necessarily so. On the other hand, the recent calculation on the oxygen molecule (156) in which a small number of Gaussian functions were used as base hardly should be considered definitive.

It seems just a little too early to attempt a detailed appraisal of prospects for theoretical calculation of dissociation energies. In his admirable new book on bond energies (168), Cottrell has indicated that quantum-mechanical calculation of dissociation energies is out of the question. This seems too pessimistic a view; it will be no mean job, but the dissociation energy of CO to an accuracy sufficient to fix the heat of sublimation of carbon should fall to brute-force quantum-mechanical calculation within the next few years; and if the patterns of error which are beginning to show in the calculations on first-row hydrides hold up, it may become possible to make useful quantitative predictions even with simpler theoretical methods.

Hybridization and the spatial distribution of electrons.—The importance of hybridized atomic orbitals in chemical bonding has long been recognized (1). The main qualitative interest of late has been in the role of *d*-orbitals. Following Mulliken in the use of the overlap integral as a criterion for bond strength (169), several authors have examined in detail compounds involving second and higher-row elements (170, 171, 172). The more quantitative studies have dealt with hybridization and ionic character as related to and determined by nuclear quadrupole couplings (173, 174). A new method for ascertaining degree of hybridization, application of a condition of "maximum penetration," has been suggested and studied by Fischer-Hjalmars (175).

Linnett & Poë (176) and Linnett & Mellish (177, 178) have shown that in the ground states of a number of isolated atoms, the most probable angles which the unpaired electrons subtend at the nucleus are closer to the valence angles than heretofore realized. Thus for the ^3P ground state of the oxygen atom (which approximates the V_2 valence state of oxygen in H_2O), the unpaired electrons are most likely to be found at an angle 103° with respect to one another, not the 90° generally supposed. Wu (179) has argued convincingly that such considerations cannot be made the basis for a theory of directed valence, however. A valence-bonded methane molecule without hybridization would have little stability.

Central in most discussions of the spatial distribution of electrons in many-electron systems is the idea of "shell," and one might wonder whether it retains its significance when one goes beyond simple orbital descriptions to exact wave functions. Naturally it does; even with exact wave functions one

has regions of space where some electrons are likely to be found, others not so likely. Such regions have been called "loges" by Daudel and his associates and investigated by them in several cases for which accurate wave functions are available (180, 181, 182). Thus, for the $1s2s\ ^3S$ state of the helium atom, the probability that one electron and one only will be found less than a distance R from the nucleus is a maximum, 0.93, when $R=0.90$ Å; the space within a sphere of this radius is one loge, which may be identified with the K-shell, the space without is another, which may be identified with the L-shell (180).

The Atomic Valence State and the Valence Bond Method

The atomic valence state.—As part of a review paper entitled "Atomic Valence States and Chemical Binding," Moffitt (183) has given a unified treatment of the atomic valence state—its definition, its role in molecular theories, and methods for evaluating its energy from atomic spectroscopic data. He points out that the valence state cannot be defined without reference to some particular molecular theory. The valence state in common use is a state of an atom in a molecule which is described by a valence-bond or perfect-pairing molecular wave function built from atomic orbitals. This state of the atom is a hypothetical state which does not, in general, correspond to any spectroscopic state of the atom. However, the valence-state wave function may be expressed in terms of spectroscopic-state wave functions if the latter are written in orbital approximations. Hence, valence-state energies can be determined uniquely from spectroscopic energies. Moffitt gives tables to facilitate such energy calculations; these supplement and remove certain ambiguities in tables of Mulliken (184), as recently brought up to date by Skinner & Pritchard (185).

New developments in the valence bond method.—In a valuable series of three papers (4, 39, 162), McWeeny has revived the lately somewhat neglected valence bond theory.

The troubles with the traditional valence bond method are two: numerous integrals that arise from the nonorthogonality of atomic orbitals are neglected in an apparently inconsistent way, and ionic contributing structures are ignored or improperly treated. McWeeny proposes a new "valence bond" theory which has neither of these disadvantages. He suggests replacing the actual nonorthogonal atomic orbitals (AO's) in a molecule with Löwdin's (38) orthonormalized atomic orbitals ($\overline{\text{AO}}$'s), and he extends the rules for computing matrix elements between valence-bond structures built from $\overline{\text{AO}}$'s to the most general case of structures with arbitrary degrees of ionicity. No special difficulty is met in working with this generalized valence bond theory. In a given problem, integrals may be computed purely theoretically or empirically as desired, and the description may be improved indefinitely by addition of more and more contributing structures.

The valence-bond structures of McWeeny are $\overline{\text{AO}}$ analogues of the conventional AO valence-bond structures, but the physical meaning of "struc-

ture" is lost in the new formulation. Resonance among the "covalent" structures built from $\overline{AO}$'s gives no binding whatever! However, McWeeny does show how to transform from one set of valence-bond structures to the other, so that one may start from a set of AO structures, transform these to $\overline{AO}$ structures, mix the latter by quantum-mechanical calculation, and transform back to the original structures.

Conclusion

There have been numerous recent studies of special types of chemical bonds. For example, Eberhardt, Crawford & Lipscomb (186) have systemized a large amount of structural information on the boron hydrides via the two-electron three-center bond, deHeer (187) has initiated studies of conjugated sulfur compounds, and Moffitt (188) has qualitatively elucidated the electronic structure of ferrocene and related molecules. Molecular complexes continue to receive attention.

The scientific contributions of the late Sir J. E. Lennard-Jones drew to a close in 1954 with the publication of the research work of two of his last students, Manning (189) and Hurley (143, 190). Physical chemistry owes much to Lennard-Jones.

No mention has yet been made of one development in valence theory which is of utmost importance, the use of electronic computing machines. Neither the steady advances in fundamental theory of small molecules that are being made by Boys nor the manifold predictions of spectroscopic states of polyacenes that have been made by Pariser would have been possible without the use of these machines. Boys and Pariser have used very similar techniques. Not just arithmetic but complete theoretical procedures can be programmed for electronic computers; as predicted by Mulliken in 1947 (191), this will be the way in the future.

Concerning the fundamental theory of small molecules, it has been said that there would be no interest in exact quantum-mechanical calculations for more than a few, because exact wave functions for many-electron systems cannot be easily interpreted. It would seem rather that new methods for interpretation will be found to meet the stiffer demands of better mathematical theory.

Concerning the theory of large molecules, it should be noted that the amount and variety of new experimental data being accumulated, paramagnetic resonance absorption data, nuclear quadrupole coupling data, and so on, make imperative a refinement of present methods of interpretation at least to the point that these data may be accounted for. That this refinement will be accomplished seems probable; a sign that bodes well for progress in this direction is the new emphasis on the idea of "model." Thus in addition to the free-electron model and the generalized Hückel model for complex unsaturated molecules, discussed above, one now has the "smoothed potential theory of chemical binding" of Arnold (192) and the "delta potential function model for electronic energies of molecules" of Frost (193).

The proceedings of an international symposium on molecular physics held in Japan in 1953 are now available (194), and a collection of Japanese contributions to the understanding of molecular structure and related problems has been published (195). The steady increase of Japanese research in this field is heartening.

As for books concerned with valence, Coulson's excellent introductory treatment has been reprinted (196), and a work by Hartmann in German also has appeared (197). But there still remains a pressing need for an advanced critical monograph on the quantum theory of valence.

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ELECTRONIC SPECTROSCOPY[1]

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An annual review on the vast field of electronic spectroscopy can obviously not be exhaustive. To the regret of the reviewer, certain important chapters had to be omitted, e.g., spectroscopy of solids and flame spectroscopy, which deserve special reports. Still more regrettable is the fact that a discussion on atomic spectra had to be taken out, again to conform to space limitations, so that only a few remarks on this important field remain. Spectra of diatomic molecules have received more attention in this review than in previous ones because of considerable recent progress in this field. Although the greatest share of space was devoted to polyatomic molecules, only examples could be selected from the enormous literature, and it is inevitable that the choice may be influenced by the reviewer's personal interest. In general, emphasis is placed upon experimental results and their interpretation rather than upon the theory of electronic levels and spectra which will be mentioned only briefly. Information on this subject is contained in the review by Parr and Ellison.[2]

Atomic Spectra

The Rydberg Centennial Conference held in July, 1954, at Lund, Sweden, symbolized the steady progress of atomic spectroscopy. The papers given represent an interesting cross-section of recent advances: improvements in the equipment (mainly high resolution, i.e., étalons, photoelectric methods, light sources, etc.); developments of recent methods (for instance, combination of optical and microwave methods), both of which have influenced new papers on hyperfine structure; Zeeman and Stark effects, line intensities, extension and revision of previously known spectra, pressure effects, etc., and more complete knowledge of accurate term values of atoms and of precise atomic electronic wave functions (atomic orbitals). For an excellent review of this Conference see Garton & Bovey (1). In general, an understanding of the spectroscopic behavior of polyatomic molecules is largely based on studies and interpretations of the simpler corresponding processes in atoms and diatomic molecules. The theoretical physicist or chemist needs accurate atomic term values in semiempirical molecular calculations, and he builds up his molecular electronic wave functions (molecular orbitals) from atomic orbitals. In Slater's (2) modification of the Hartree-Fock self-consistent field method the exchange terms of the N integro-differential equations are replaced by a simple average exchange potential. Hence, only one equation

[1] The survey of the literature pertaining to this review was concluded in January, 1955.

[2] The author is indebted to Dr. Parr and Dr. Ellison for permission to see a copy of their review.

needs to be solved in each approximation order. This is simpler than even the (exchangeless) Hartree method. Applications to Cu^+ compare favorably with the Hartree-Fock treatment [Pratt (3); Morrow (4)]. Löwdin (5) has shown that Slater's method can be justified theoretically and suggested an extension to molecules. An exchange potential different from Slater's has been proposed recently (6). Configuration interaction, needed to account for electronic repulsion terms has been used by Yutsis and co-workers (7, 8) for atoms of the type He, and Be, and by Green et al. (9, 10) for He and isoelectronic sequences. Impressive work was reported by Boys & Price (11) for Cl, Cl^-, S, and S^-, incorporating even relativistic effects. A few papers deal directly with the Bacher-Goudsmit theory of complex spectra. In this theory the energy of an atomic state is expressed as a linear combination of the energy levels of the ions of that atom. Trees (12) tested the theory in the spectra of *d* and *s* electrons. He showed that the B-G theory can be interpreted in terms of a "linear theory" in which the $L(L+1)$ correction (influence of polarization) is combined with the Slater theory and in which the radial integrals (parameters) are given by series expanded in the degree of ionization. This paper by Trees is the latest in a series of developments in the theory of complex spectra. Other contributions were by Racah (13), Catalan, Roiirlich & Shenstone (14), Meshkov & Ufford (15, 16), and Gehatia (17).

It is of interest that in 1954 the gap between microwave and optical regions has been bridged; from the microwave side by Burrus & Gordy (18) and from the extreme infrared by Genzel & Eckhardt (19).

Diatomic Spectra

As in the case of atomic spectra, some work was devoted to extension into other wave length regions, notably into the vacuum ultraviolet where comparatively little had been known of the spectra of simple molecules. New methods and improved techniques such as the use of multiple absorption paths, methods of flash photolysis, excitation in hollow cathode discharges, flame-spectroscopic methods, etc., aided in the accumulation of new data and in increasing the accuracy of previously obtained values. Rotational analyses were given for a number of band systems. Intensities and transition probabilities were obtained particularly for molecules of astrophysical interest.

The absorption studies in the Schumann region were carried out by Barrow & Rowlinson in the vapors of SiO, GeO, SnO, SnS, and AlF (20) and have led to the discovery and vibrational analyses of several new band systems in these molecules. Dissociation energies, D_0, were derived in all cases. For SiS an improved value D_0 was obtained from the E–X system in emission (21). For AlF, some of the excited singlet states have also been obtained in emission (22) (hollow cathode discharge) as well as some triplet-triplet transitions (23). Rotational constants were reported for four emission singlet systems (22). The hollow cathode discharge proved also appropriate for the excitation of emission spectra of the molecules GaF and InF (24). Furnace spectra have been observed in the vapors of BiO (25) and BiSe and

BiTe (26), yielding several new absorption systems in the ultraviolet for which vibrational constants were proposed. An extensive thermal emission spectrum in the visible was obtained in a King furnace in the presence of Al. It was attributed to the AlC molecule and it is the first metallic carbide spectrum described (27). In the same King furnace the AlH band system at 4241 Å was produced at about 2100°C. both in emission and absorption and photographed in the second and third order of a 21 ft. grating spectrograph (28). The higher precision of the new over previous data gave values for the vibrational and rotational constants. Other interesting results obtained in a King furnace (at 2500°) containing samples of copper, silver, and gold were reported by Ruamps (29) and Uhler (30). Six new band systems were found in emission in the region 3800 to 5300 Å and assigned to Cu_2, Ag_2, and Au_2. A vibrational analysis was carried out for 5 systems. Observation and calculation of the isotope effect in the copper and silver spectra support the assignment. When the furnace was loaded with a Cu-Au alloy four systems of unknown bands were observed and attributed to the molecule CuAu (31).

New results have been reported, mostly from the Swedish group of Lagerqvist, Huldt *et al.*, on the oxides of the following elements: Be, Ca, Sr, Ba, Ni, Ag, Mo, Nb, and Zr. Improved values of dissociation energies D_0 have been given for the first four oxide molecules (32, 33). An upper limit was found for NiO (34). The D_0 values, except for BeO, were derived from photoelectric intensity measurements of atomic lines and bands in flames (35). The new measurements showed conclusively that the ground states of CaO and SrO are $^3\Sigma$ states and that the visible bands of these oxides occur between excited states. This is in agreement with conclusions reached for MgO by Brewer & Porter (36) in a detailed thermodynamic and spectroscopic study of this molecule. Vapor pressure determinations of MgO derived from intensities of temperature emission of the green MgO bands could only be reconciled with the thermochemical determination if the lower $^1\Sigma$ state of these bands lies considerably above the ground state. The authors conclude that the ultraviolet MgO bands combine with a $^3\Sigma$ ground state. Brewer had mentioned earlier (in *Chemical Reviews*, 1953) that the gaseous alkaline earth oxides may have triplet ground states. It seems rather certain, though, that BaO has a $^1\Sigma$ ground term (35). Detailed rotational analyses were presented for several bands of the ultraviolet systems of CaO (36a), SrO (37), the blue bands of SrO (38, 39), AgO (40), and NbO (41). Uhler analyzed the NbO system as $^2\Delta - {}^2\Delta$ transition which is at variance with an analysis by Rao (42). From a rotational analysis of the 0,0 bands of the α- and γ-systems of ZrO, Lagerqvist, Uhler & Barrow (43) concluded that they represent triplet systems. Rotational analyses of some bands of the β-system of the NS molecule led to the assignment $^2\Delta - {}^2\Pi$ replacing the previous assignment $^2\Pi - {}^2\Pi$ for this system (44). Observation of 10 band systems in MoO vapor in the region 9000 to 4500 Å was announced in (45) with no analysis given. New emission bands were observed (46) in the region 7200 to 8000 Å in a discharge through flowing NO gas and were tentatively assigned to a $^4\Sigma - {}^4\Pi$

transition of NO predicted by Mulliken. Three new absorption systems were found in BiBr vapor (47).

Three new band systems of CaCl were discovered in the positive column of a discharge through Ca-$CaCl_2$ vapor and analyzed, region 5500 to 4600 Å. Electronic energies and vibrational constants of all known CaCl levels were tabulated (48). In a hollow cathode discharge through He and C_2N_2 six new band systems were observed at 4500 to 1900 Å. Two of them were attributed to $^1\Sigma - ^1\Sigma$ transitions of the CN^+ molecule, and rotational analyses were given, thus furnishing the first spectroscopic evidence of this ion which is of considerable astrophysical interest. The other four systems belong to CN involving some new states (49). As discussed repeatedly, the emitters of spectra observed in hollow cathode discharges are often difficult to identify. For example, renewed effort was made to establish the carrier of such a system which had been found by Schüler at 5500 to 4200 Å and was attributed by him to OH. Benoist (50), using higher dispersion, was able to locate the origins of several bands and to give plausible reasons for the system being a $^2\Sigma - ^2\Sigma$ transition with oxygen being one atom in the diatomic emitter. Assuming it to be OH, approximate locations of the levels were suggested. In another case, the emitter, presumably a diatomic hydride of an interesting spectrum obtained in a hollow cathode discharge through hydrogen and potassium fluoride is still unidentified, though a rotational analysis was made (51). A strong but, until recently, undetected auroral emission has been identified as the 1-1 band of the $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ system (atm. bands) of O_2 (52).

A rather exhaustive study of the ultraviolet fluorescence spectra of I_2 has been reported in (53). With new wave lengths measurements and four new electronic states identified, I_2 is one of the spectroscopically best known molecules. Extinction coefficients were measured in the vacuum ultraviolet absorption spectra of I_2 and Br_2 (54). Contrary to usual findings, higher intensities were noticed in the gas than in the solution spectra. Possible explanations are being examined. Another extensive investigation is being carried out by Dieke and his collaborators (55) on the molecular spectra of hydrogen and its isotopes (H_2, DH, D_2, TH, TD, and T_2). Several papers of interest have appeared on spectra of O_2. The forbidden $^3\Sigma_u^+ \rightarrow ^3\Sigma_g^-$ system (Herzberg bands) has been extended by producing it in emission (phosphorescence) in an afterglow of flowing oxygen in an uncondensed discharge. Comparison was made with the night-sky spectrum, in which this system appears (56). Absorption bands caused by interaction between oxygen molecules were studied at ordinary temperature as function of their self-pressure up to 1500 atm. in (57), and in (58) approximate absorption coefficients were briefly presented of solid oxygen at 2000 to 1500 Å. The Schumann-Runge bands were the object of three papers which, in a way, supplement each other. In (59) interest centered around the problem of explaining the simultaneous emission of the Schumann-Runge bands $B^3\Sigma_u^- - X^3\Sigma_g^-$ and the forbidden OI lines $^3P - ^1D_2$ when oxygen is excited at atmospheric pressure (high voltage discharge). Transition probabilities (using distorted harmonic oscillator

functions) were calculated for the band region 2600 to 6600 Å, and the various photochemical reactions that are possible were discussed. Weniger & Herman found thermal distribution for normal molecules and O^3P and O^1D atoms, but the population of $O_2B^3\Sigma$ molecules is much smaller than for thermal equilibrium. Vibrational transition probabilities were also calculated for the Broida-Gaydon system $^3\Sigma_u^+ - {}^1\Sigma_g^+$ and the atmospheric bands $^1\Sigma_g^+ - {}^3\Sigma_g^-$ of O_2 and compared with visual estimates from the published experimental data (60). The paper by Ditchburn & Heddle (61) contains absorption cross-section measurements in the 2000 to 1750 Å region of the Schumann-Runge bands. From these, oscillator strengths were calculated for the vibrational transitions. The total f value was found to be 0.259, and the dissociation limit is given as 57140 ± 20 k. Brix & Herzberg (62), in a detailed and extended fine structure analysis of all bands with $v' > 11$, using high resolution, were able to fix this value as $57128 \pm 5k$, thus obtaining for the dissociation energy of oxygen $41260 \pm 15k$, or $5.114_8 \pm 0.002$ ev or 117.96 ± 0.04 kcal./mole. The new value is 0.63 per cent higher than the old one. In contrast, the value of the dissociation energy of nitrogen can still not be regarded as entirely settled although $D_0 = 9.765$ ev is now almost certain (63). It was supported by a recent experiment in which N_2 was dissociated thermally (64). With this value and the new $D_0(O_2)$ the energy of dissociation of NO becomes $D_0(NO) = 52477 \pm 50$ cm.$^{-1} = 6.505_2$ ev $= 150.0_3$ kcal./mole (62). This value is again corroborated in a recent study by Tanaka (65) of the emission bands of NO in the vacuum ultraviolet region excited in an impure nitrogen-oxygen afterglow. The fact that Gaydon & Fairbairn (66) could not establish an abnormal pressure broadening in the γ-bands of NO and hence an induced predissociation, as had been reported and suggested, is another point for the quoted values. Although a dissociation heat of nitrogen of 9.765 ev fits into schemes of bond energies [see, for example, (67)], it must be kept in mind that similar or other relations may be derived using a different value [see discussion in (68)]. It is, therefore, important that recent considerations on the mechanism of the Lewis-Rayleigh afterglow of active nitrogen (69, 70) also lead to $D_0(N_2) = 9.76$ ev. In this theory, the old idea (71, 72) that the recombination of two normal ^4S N atoms furnishes the energy necessary for the afterglow, was re-examined by performing new experiments and discussing thoroughly the possible collision (triple) processes. The only new observations which speak for the value $D_0(N_2) = 7.373$ ev are Lindholm's results (73) on appearance potentials and collision (N_2 and atomic ions) cross-sections by a mass-spectroscopic method. The experimental technique is elegant and the conclusions are plausible; still, they are not entirely convincing and the optical results just mentioned are favored by the reviewer. It may be added that Lindholm, using the same method, deduced 9.605 ev for $D_0(CO)$ and correspondingly 135.7 kcal./mole for the heat of sublimation of carbon (74). F_2 is another molecule which received considerable attention on the question of its dissociation energy and electron affinity. The methods are nonspectroscopic but are included because of the interest in the results. Sanderson (75)

concluded, from curves relating D_0 values of diatomic gas molecules of elements of the different groups to the principal quantum numbers of the valence shells, that a low value of $D_0(F_2)$ like ~40 kcal./mole seems improbable. A new determination by the effusion method (76) gave $\Delta H^\circ_{298} = 37.6 \pm 0.8$ kcal./mole for the dissociation reaction, thus confirming previous values calculated from thermochemical data and obtained from measurements of the pressure variation with temperature. Quantum-mechanical calculations (77), although they cannot be cited as confirmation of any special value, seem to support a low value of the binding energy of F_2 since such calculations usually give rather too high than too low values. The electron affinity of F_2 was recently calculated (78, 79) by means of the Hellmann-Mamotenko extrapolation method in which the average removal energy per p electron was extrapolated (from spectroscopic data) to the atom or ion with one more p electron. Result $E(F_2) = 78.6$ kcal./mole which is a few kcal. lower than the experimental value 82.2 ± 4 kcal./mole (80, 81). It was pointed out that, while such extrapolations in series of positive ions have given excellent results, this is not to be expected for extrapolations to negative ions whose electronic structure is more different than that of successive preceding members of the series. An extensive spectroscopic study of HF has been carried out by Safari (82), in which the absorption of the gas was examined in the ultraviolet and the Schumann region, the infrared spectrum in gaseous and liquid HF, the Raman spectrum in the liquid. HF gas was found to be transparent in the middle and near ultraviolet up to 225 cm. thickness and 760 mm. pressure, and the first absorption region appeared at 1650 Å. The potential curve of this state was discussed, and the effect of the temperature on the spectrum explained by means of molecular association.

A fairly large group of papers is concerned with the evaluation of vibrational transition probabilities in electronic band systems, particularly for molecules of astrophysical interest. Methods of calculating these probabilities vary according to the approximations used [see discussion in (83, 84)]. The harmonic oscillator is the simplest model but it is not suitable for higher vibrations. Consequently, "distortion" methods have been developed for obtaining approximate vibrational wave functions for a Morse potential from those of the harmonic oscillator and they have been applied to numerous molecules (Pillow). Secondly, the electronic transition moment $R_e(r)$ is constant in first approximation only. Assuming that $R_e(r)$ is practically independent of the internuclear distance or a very slowly varying function of r, values of squares of the overlap integrals $\int \psi_v, \psi_{v''} dr$ have been computed for a number of molecules (N_2^+, N_2, CN, C_2, O_2, and TiO) (85, 86). How valid the assumption of constancy of $R_e(r)$ is, was tested (87) by securing experimental intensities $I_{v'v''}$ and obtaining from them relative values of $\left|\int \psi_{v'} R_e(r) \psi_{v''} dr\right|^2$ for bands of the first positive system of N_2. These values were then compared with the overlap squares $\left|\int \psi_{v'} \psi_{v''} dr\right|^2$ calculated in (86). For the introduction of the dependence of R_e upon r the reader is referred to (88) and (89). In the particular case of the first positive N_2 system

($B^3\Pi_g - A^3\Sigma_u$), it was found that over the range $1.17 < r < 1.59$ Å of internuclear distance, this dependence may be represented by $R_e(r) = \text{const.}\ e^{-3.02r}$. The intensity distribution of the same N_2 system was also determined from its emission in a discharge lamp and compared with Vegard's intensity measurements in the aurorae (90). In (91) calculation was made of the way in which visual estimates of band intensities can be used in some cases for an approximate evaluation of $R_e(r)$ dependences. A different method which uses recurrence relations for the calculation of overlap integrals had been suggested by Manneback. It was extended (92) to include the $R_e(r)$ dependence upon the internuclear distance, while the mechanical harmonicity of the two electronic potentials was preserved. Another paper (93) dealt with a careful determination of relative transition probabilities of a number of bands in the α-system of TiO which was excited in an electric furnace at temperatures between 2100 and 2600° K. The spectrum was scanned photoelectrically. Relative intensities were obtained by matching observed band profiles with profiles determined theoretically. Premaswarup (94) has continued his calculations of intensity factors for the rotational branches in high multiplicity bands, this time for $^6\Pi - {}^6\Sigma$ and $^6\Pi - {}^6\Pi$ transitions.

The hydrogen molecule and its ion, being the simplest polyatomic systems, have always been test cases for various theoretical treatments. Consequently, a number of papers appeared during last year on these molecules. Most of them will be omitted because of space limitation, and the reader is referred to Parr & Ellison's article. Only a few can be mentioned. One is written by Kockel (95) who, after reviewing a number of previous trial wave functions for H_2, concluded that elliptical coordinates give the best results. A relatively simple wavefunction in these coordinates was shown to be superior to all approximate functions tried, with the notable exception of the James-Coolidge function, which also had been expressed in elliptical coordinates. Berencz (96) took a Weinbaum (covalent plus ionic) wave function multiplied by a correlation factor $(1 + pr_{12})$ for the H_2 molecule. The result, however, represents only a slight improvement over the less complicated "correlated orbitals" of Frost & Braunstein which did not contain the ionic term. Kuhn and co-workers (97), in treating H_2^+, employed free electron gas wave functions along the molecular axis. For both the $1s\sigma$ and $2p\pi$-states, two parameters were varied. Comparison with the LCAO method without parameters proved their method to be inferior for the $1s\sigma$-state, but superior for the $2p\pi$-state. Schäfer (98) showed, however, that this superiority vanishes if an effective charge parameter is introduced in the LCAO treatment.

Quantum-mechanical calculations have also been carried out for the following diatomic molecules: Li_2 [Rahman (99)], CH [Higuchi (100)], LiF [Benson & van der Hoff (101)], and O_2 [Ohno & Itoh (102)], aside from F_2 mentioned previously. Mizushima (103) has completed a detailed theoretical treatment of the $^2\Pi$ ground state of the NO molecule. This was instigated by recent hfs and Zeeman observations (104, 105). He concluded that the

ground level is essentially $^2\Pi_{1/2}$, but has slight admixtures of $^2\Pi_{3/2}$, the next $^2\Sigma_{1/2}$ and a very small amount of the electronically-excited $^2\Pi_{1/2}$ state.

Polyatomic Spectra

Part of the literature discussed in this review represents publication of papers given at the Réunion Internationale de Spectroscopie Moléculaire in June-July, 1953, at Paris, France, the International Conference on Theoretical Physics at Nikko, Japan in September, 1953, and at the Symposium on Molecular Spectroscopy in June, 1954, at Columbus, Ohio. Such meetings, in which all branches of scientists interested in spectroscopy come together, are not only important because of ensuing personal discussions but collected papers of such conferences bear excellent witness to the progress in the field. The papers of the Paris Conference, for example, have appeared in book form in 1954.

Simpler Molecules.—Douglas (106) had suggested that the λ4050 bands, which were first observed in the spectrum of comets and later reproduced from laboratory sources, may arise from a $\Sigma-\Pi$ transition of a linear C_3 molecule, and he presented a rotational analysis of the strongest band. To establish the emitter of the bands, they were excited (107) with the pure C^{13} isotope and photographed under high resolution. The lines of the strongest band show a 3:1 intensity alteration. A reasonable analysis consistent with that of the C^{12} band was obtained on the assumption that the B values of the C^{13} band are 12/13 of those of the C^{12} band. Comparison of this with previous work with 50 per cent C^{13} in which six band heads were observed leads to the conclusion that the molecule contains three carbon atoms. This makes it practically certain that a C_3 molecule is the emitter. The analysis of the C_3^{12} molecule has been extended by Kiess & Bass (108) who obtained the λ4050 group in the acetylene-oxygen flame. Studies of the absorption spectra of N_2O and NO were reported by Granier-Mayence, Romand & Robin (109). The broad maximum of N_2O gas at 1830 Å shifts to 1780 Å in the solid. Another maximum at 2120 Å at 20°K. was suggested as due to photodecomposition (probably NO). For NO, the strong maximum at 2100 Å at $T=20$°K. was attributed to a transition $N_2O_2\rightarrow 2NO$, a minimum appearing at 5300 Å in compressed NO (800 atm.) was connected with N_2O_3. The fluorescence of NO_2 excited by visible light has been studied several times, but the results have been partly conflicting and have not let to unambiguous conclusions on position and lifetimes of the excited states of this molecule. The new paper by Neuberger & Duncan (110), although giving some interesting information, did not succeed to reach a final solution. To establish the emitter of the α-band of ammonia, spectra of NH_3 and ND_3 were obtained in a Schüler-type discharge (111) and compared with spectra of the N_3H-explosion flame and the NH_3/O_2 flame. The λ4485 band was assigned as 0,0 band of the $^1\Pi-{}^1\Sigma$ ND transition, and λ5205 was attributed to ND_2. The α-band of ammonia was interpreted as $^2A_1-{}^2B_1$ transition of the radical NH_2. The absorption band of water vapor at λ1600 − 1700, which

shows several peaks, was considered to belong to the decomposition $H_2O \rightarrow H + OH$ (112). Duchesne has examined the vibration potential functions of the ground and first excited states of phosgene $COCl_2$ (113) and of thiophosgene $CSCl_2$ (114). Analysis of the respective absorption spectra supplied several vibrations in the excited levels of these molecules, ground state vibrations were taken from Raman and infrared studies. A very general potential function was used and the symmetry C_{2v} was preserved in the calculations for both states involved. Force constants and internuclear distances were obtained and some interesting conclusions drawn, e.g., relationships between the CO and CS bond strengths and antibonding power of the π^* electron, degree of localization of the π^* orbital in the two molecules, role of the lone-pair electrons for the ClCCl angle. The absorption system of *trans*-glyoxal at 4500 to 3700 Å was interpreted by Brand (115) as an (allowed) $^1A_g - {}^1A_u$ transition. The "forbidden" part of the spectrum involves a nonplanar β_g-vibration. The vibrational structure was discussed using emission and absorption data of glyoxal and glyoxal-d_2. Partial rotational analysis of some bands confirmed the planar *trans*-structure in both combining states. A much weaker transition at 5200 Å was considered to be probably a singlet-triplet intercombination. Nostrand & Duncan (116) have measured absolute intensities of four separate transitions of SF_6 between λ1850 and λ780 Å. The f values for three of them, which belong to a Rydberg series, are: $f = 0.294$ (λ1057), $f = 0.13$ (λ870), $f = 0.097$ (λ817). Ionization limit of the series is 16.15 ev. Pressure broadening of rotation lines by added rare gases was used to smooth out the absorption. Measurements of the same type were made for acetylene and deuteroacetylene. Ingold & King's work (117, 118) on the interpretation of the near ultraviolet system of acetylene at 2470 to 1970 Å was confirmed and somewhat extended by Innes (119), who photographed the bands under high resolution with absorbing paths of 0.007 to 70 m-atm. The upper electronic state is bent and has C_{2h} symmetry, the state being A_u or, possibly A_g. The analyses of the authors agree. The 0,0 transition was located at 42197.69 cm.$^{-1}$. The effective moment of inertia of the excited state was found to be small causing sub-band separations of 50 to 150 cm.$^{-1}$. The sub-bands form progressions of the bending vibration $\nu'' = 611.7$ cm.$^{-1}$ in the ground state and $\nu'(CCH) = 1047.70$ cm.$^{-1}$ in the upper state. The angle of the bent molecule is $\sphericalangle CCH = 120°$. Reinebeck & Schüler (120) described a spectrum at 6500 to 4675 Å appearing in a hollow cathode discharge through diacetylene. A vibrational analysis was made involving frequencies which agree closely with known ground-state frequencies of this molecule, but it was not possible to find a corresponding absorption system. The authors had observed the same spectrum (T spectrum) previously in discharges through certain aromatic vapors with He as carrier gas. In spite of various efforts, the emitter of this spectrum must still be considered uncertain. Pickett & Carr and their co-workers continued their studies of far ultraviolet absorption spectra of saturated hydrocarbons. Peak positions and intensities were measured from 45,000 to

64,000 cm.$^{-1}$. of the isomeric butenes (121), the isomeric pentenes (122) and selected isomeric hexenes (123). All spectra show a broad intense band (Mulliken's N—V transition) and superimposed systems of narrow bands, both at longer and shorter wave lengths (N—R bands in Mulliken's notation). The N—R bands (Rydberg bands) shift with the number of alkyl groups adjacent to the double bond, but the broad maximum was found to lie at longer wave-lengths when the resultant dipole moment was in the direction of the double bond than when it was perpendicular to this bond. Furthermore the molecular shape was important for intensity and energy of the N—V band. Oscillator strengths for this bond have been reported for six pentenes (122).

Quantum mechanical calculations on energy levels of the following simple polyatomic compounds have appeared last year: H_2O (124), NH_2 (125), NH_3 (126), HCN (127), C_2H_4 (128, 129), diacetylene (130), butadiene (131, 132, 133), and cyclobutadiene (134). For details see Parr and Ellison's review.

Simpler aromatic molecules.—Several papers have appeared on simpler derivatives of benzene and of pyridine. Wenzel (135) has suggested that nitrobenzene has its first π-electron transition at about 34,500 cm.$^{-1}$ and that it is hidden by the strong absorption band at 40,000 cm.$^{-1}$ (values refer to solution data). The two transitions were set in parallel with the first two electronic systems in benzene, and the weak band at 26,800 cm.$^{-1}$ was assigned to excitation from the NO_2 group. The hidden nitrobenzene band shows up in the spectra of *o*- and *m*- halonitrobenzenes (136), but is covered by the 2600 Å system in the *p*-halonitrobenzenes. From the discussion presented by Ungnade it is concluded that the band is considered the analogue to the weak 2600 Å system in benzene. In connection with the existence of hidden bands, an interesting investigation by Beale & Roe may be mentioned here of possible hidden transitions in the near ultraviolet absorption bands of stilbene and substituted stilbenes (137). Results on wave length shifts of the first electronic transition (0,0 bands) of a number of simple fluorinated benzenes were presented and briefly discussed in (138) in relation to the inductive and migration effects. A detailed analysis of the near ultraviolet spectrum of *p*-difluorobenzene (some 600 bands measured) was presented by Cooper (139). The system is an $A_{1g}-B_{3u}$ transition with 0,0 band at 36,843 cm.$^{-1}$, and *f*-value 0.022 (138). Force constants of the C—C and C—F bands and the CCC angles in the ground and excited states of this system had been discussed before (140) with a brief description of the spectrum. For *o*- and *p*-bromotoluene two broad fluorescence bands in the visible were reported (141) when the liquids were cooled to −180°C. Spectra taken at −60°C. do not show any trace of fluorescence. Similar fluorescence bands appearing at −180°C. had been observed before for chlorotoluene and polystyrene (142, 143).

The near ultraviolet absorption spectra (region 34,000 to 48,000 cm.$^{-1}$ of the following substances have been measured by Stephenson (144) in *iso*-octane and ethyl-alcohol solutions: pyridine, the isomeric picolines, 2- and

3-fluoropyridine, 2- and 3-chloropyridine, and 2- and 3-bromopyridine. For pyridine, the picolines, and the 3-halogenpyridines, the first systems (singlet-singlet $n-\pi^*$ transitions) decrease in intensity when the solvent is changed from *iso*-octane to alcohol, while the second systems (singlet-singlet $\pi-\pi^*$ transitions) gain in intensity. No intensity changes occur in the low-energy regions for the 2-halogenopyridines. In fact, the $n-\pi^*$ transistions of these substances were absent in this region. This was explained as inductive attraction of the halogen attached to the carbon atom adjacent to the nitrogen which increases the binding energy of the nonbonding electrons existing in pyridine. The transitions are probably shifted into the region of the $\pi-\pi^*$ absorption. Oscillator strengths were measured for both type transitions, and it was noted that Sklar's vector moments addition rule does not apply to the $n-\pi^*$ transitions. Andon, Cox & Herington (145) presented the absorption spectra and thermodynamic dissociation constants at 25°C. of pyridine, the three methylpyridines, the three ethylpyridines, and the six dimethylpyridines in aqueous solution. Wave lengths and extinction coefficients of the absorption peaks, and the dissociation constants were tabulated. Several general relationships were deduced concerning the effect of molecular structure on the spectra of pyridine bases in aqueous solution. Hirt and collaborators (146) have measured the near ultraviolet absorption of *s*-triazine whose existence was verified recently (147). A strong $n-\pi^*$ transition appears at 36,780 (maximum in solution) and a weaker $\pi-\pi^*$ ($A_1'-A_2'$) transition at 45,350 cm.$^{-1}$ (solution). Search for a low-energy triplet transition ($^1A_1'-^3A_1'$) was negative in agreement with calculations by the authors (semiempirical MO method of Pariser & Parr) which put this transition in the general region of the $n-\pi^*$ system. The spectrum of *s*-triazine resembles that of 2,4,6-trimethyl-*s*-triazine. New solution data on the latter compound have been reported by Paoloni (148). Near ultraviolet absorption spectra were obtained for a large number of substituted aminotriazines and spectral changes discussed in relation to the substituents (149). As for new absorption studies in triazoles, a paper by Atkinson *et al.* (150) on ultraviolet spectra of 1,2,4-triazoles may be mentioned. The ultra violet absorption of the 2-, 3-, 5-, 6-, 7- and 8-monobromoquinolines was measured in 95 per cent ethanol. 10 per cent ethanol, and 10 per cent ethanol with 0.01 *M* hydrochloric acid (151). Extinction coefficients, wave length shifts of the maxima and dissociation constants were given, and the order of basic strengths of the different quinolines was discussed. As a last example of recent spectroscopic studies of simpler heterocyclic compounds, results may be mentioned which were obtained by Passerini & Cerniani for benzoxazole and many mono- and disubstituted derivatives (152), and for benzothiaxole and its derivatives (153). The spectra were taken in ethanol, *N*/1 aqueous hydrochloric acid, or *N*/10 aqueous sodium hydroxide solutions. Interpretations were offered on the basis of essentially localized chromophores; for example, the first and second absorption systems of benzoxazole at 2700 Å and 2310 Å, and of benzothiazole at 2850 Å and 2520 Å were interpreted in analogy to the two

first benzene absorptions, that is, without assuming specific excitation in the hetero ring. The same applies to the 2-methyl derivatives. In the nitro-substituted compounds the first system was attributed to a combined nitro-chromophore, and so on. A general bathochromic shift without intensification from benzoxazole to benzothiazole compounds, found in the bands assigned to the benzochromophore, was explained as a shift of relative conjugating power of O and S from the order O > S in the ground state of the carbon $2p\pi$ shell, towards the order O < S, as the $2p\pi$ shell becomes enlarged in the excited electronic states.

Several microwave studies of simple aromatic molecules have appeared last year: fluorobenzene (154, 155), chlorobenzene (156), benzonitrile (157, 158), and pyridine (159, 160, 161). For the last molecule, microwave spectra have also been obtained for 2-, 3-, and 4-monodeuteropyridine (159). The microwave spectrum of cyclopentanone has been investigated by Erlandsson (162). Molecular constants have been evaluated for the different molecules. Of particular interest are the results in pyridine. Duchesne & Monfils measured the quadrupole spectrum of 1,2,4-trichlorobenzene (163) and compared the results with a general representation (164) of quadrupole spectra of other chlorinated benzenes.

Recently, Robinson has been quite successful in obtaining well-developed emission spectra of some simple organic molecules. A high-frequency electrodeless discharge technique was used (165), and the gases were pumped through the discharge tube, sometimes in conjunction with a carrier gas. A spectrum of over 100 sharp bands in the region 3688 to 5433 Å was obtained for benzaldehyde and some broad emission bands were found for acetophenone. The 0,0 bands were assigned at 26,914 $cm.^{-1}$ and 27,501 $cm.^{-1}$, respectively. In acetaldehyde, a complex emission spectrum was obtained with the same technique, extending from 3500 Å into the red with a maximum at about 4200 Å. Robinson considered the acetaldehyde molecule as the emitter of these bands (166). It seems that the same system has been obtained by Régnier under very similar experimental conditions (167), and a number of band heads in the region 3750 to 5000 Å have been given. The bands appeared also in a hollow cathode discharge of the Schüler type. Régnier expressed doubt that the emitter of these bands is the acetaldehyde molecule. In discharges of the type Robinson has used, the spectra represent mostly the undissociated particles, whereas the hollow cathode discharge tends to break up the molecules and the spectra belong mostly to molecular fragments. Schüler & Reinebeck (168), in a recent survey article on emission spectroscopy of organic compounds in a low-pressure discharge (hollow cathode), have stressed this tendency and discussed the problems connected with the identification of the new spectra. (The spectrum in diacetylene vapor mentioned before is such an example.) They summarized the interesting spectroscopic phenomena which happen in low pressure and low to high energy discharges through organic vapors. In this connection a paper by Walker & Barrow (169) is of interest. These authors present good evidence that

Schüler's *V* bands belong to the fragment C_6H_5C since emission of these bands occurs by molecules containing this group, but they do not exclude entirely as emitter a form containing less hydrogen and perhaps being charged. Schüler and collaborators had also considered C_6H_5C as possible emitter but had favored the benzyl radical $C_6H_5CH_2$.

Naphthalene and derivatives.—Considerable effort has been made to obtain a better understanding of the electronic systems of the naphthalene molecule. Vibrational assignments are now available for naphthalene [Raman (170), infrared (171, 172, 173)], and such knowledge is, in general, of great aid in the interpretation of electronic spectra. The beautiful work of McClure (174) with mixed crystals of 0.1 per cent naphthalene in durene has clarified the polarization properties of the first two excited states of naphthalene. From absorption and fluorescence spectra the first transition can be considered established as $A_{1g}-B_{3u}$ with long-axis polarization and the second as $A_{1g}-B_{2u}$ with short-axis polarization. The main and much stronger part of the first system displays the characteristics of a forbidden transition (short-axis polarized) as had been noticed in the vapor spectrum before. This part is now explained by McClure as arising through an interacting β_{1g}-vibration of 433 cm.$^{-1}$ in the upper state (Sponer and Nordheim's earlier explanation of the corresponding vapor spectrum was an interacting β_{2u} vibration in an $A_{1g}-A_{1g}$ transition). In addition to this 0,1 band there is a weak 0,0 band, but no corresponding 1,0 band had been found. While it might be possible to explain this and some other features, it is not easy to suggest a reasonable Raman frequency of symmetry β_{1g} whose value could be 433 in the upper state. Indeed, Passerini & Ross (176), in a study of the temperature dependence of the first transition in solution, came to the conclusion that the 432 corresponds to the $\alpha_{1g}512$ Raman vibration. That is, to make McClure's interpretation final, a few points have still to be cleared up. A very recent and interesting investigation by Wolf (175) of the fluorescence spectrum of naphthalene in solid solution and in the crystalline state, although supplying additional data, also does not settle the remaining questions. Analysis of the second transition $A_{1g}-B_{2u}$ proved to be simpler but is also not perfect (177). Here, the interpretation of the $v'-v''$ bands (long wave-length companions of the main bands) is ambiguous, and excitation of a 485 cm.$^{-1}$ vibration in the upper state leads to a discussion on possible vibrationally induced "forbidden" bands in this system which are predicted by theory (178) but cannot be verified with certainty from the spectrum. A very good solution curve of the second transition was published in (179). Ferguson and co-workers (180, 181, 182) have examined absorption, phosphorescence, and infrared spectra of naphthalene and simple halogen derivatives in solution. Absorption curves reproduced in (180) show the different effects that α- and β-substitutions have on the second transition. Intensities and red shifts increase markedly from the fluoro- to the iodo-compound in the α-spectra, while β-substitution has much less effect. For the weak first transition the β-spectra suffer the larger red shifts. These spectra have a simple

structure and strong 0,0 bands. In the α-spectra, which are more complex, the 0,0 transition gains in intensity from iodine- to fluorine-substitution. An upper state frequency of mean value 470 in the β-spectra was linked with the α_{1g} 512 Raman fundamental of naphthalene and one of about 430 cm.$^{-1}$ in the α-spectra with the 473 fundamental which was observed strongly in the infrared spectra of monohalogen naphthalenes and was related to the 478 fundamental in naphthalene (181). These assignments demonstrate again the existing difficulties. The absorption spectra of α-chloro- and α-bromonaphthalene were also examined by Deb (183) in the vapor, liquid, and solid states, and analyses were presented. Phosphorescence spectra of naphthalene and the monohalogen derivatives in rigid petroleum glass taken with a photomultiplier technique (182) supplement very nicely the mentioned spectroscopic studies. The strong appearance of the 1575 cm.$^{-1}$ frequency in the phosphorescence spectrum can now be explained since it was reassigned to a symmetric mode (170, 173). The excited state of the naphthalene phosphorescence was given as probably $^3B_{2u}$. The relation between the point-group symmetry of the molecule and the appearance of the phosphorescence spectrum of the different compounds was discussed. Singlet-triplet absorption bands have been reported by McClure and co-workers (184) for a number of halogen benzenes and naphthalenes. Triplet state life-times were given and values of the nonradiative transition rates from triplet to ground state were derived. The effect of the atomic number of a substituted halogen atom on the absorption intensity was considered. No additivity of the spectroscopic moments of substituents was stressed for singlet-triplet transitions.

More complicated molecules.—Lippert (185) studied spectral position and relative intensity of the fluorescence maximum of nitro-compounds of the type $X—R—NO_2$ in solutions in dependence upon the constitution of the compounds and upon the solvent. It was found that the capacity to fluoresce becomes negligibly small or vanishes as soon as the energy available for exciting the fluorescence surpasses the dissociation energy of the bond $R—NO_2$. (X = electron donor, R = unsaturated rest). Fluorescence quenching occurs then as a consequence of the dissociation process which competes for the utilization of the excitation energy. Franck & Levi's (186) explanation of the cause of this competition has been used, namely the assumption, that in complex molecules a triplet state belonging to a repulsion curve of the weakest bond may be energetically close enough to the excited state so that a radiationless transition into this triplet state could be brought about by a small thermal fluctuation. Furthermore, the positions of absorption and fluorescence bands of a number of substituted nitrostilbenes have been measured for a large number of different type solvents (187). Using *p*-nitro-*p'*-dimethylamine stilbene as an example, the smaller shift of the absorption when going from saturated hydrocarbons as solvents (cyclohexane) to substituted aliphatic ones (methanol), then to aromatic hydrocarbons (benzene), and finally to substituted aromatic solvents was compared with the much larger shifts of the fluorescence spectra. The difference $\nu_{abs} - \nu_{fl}$ increases

with the dielectric constant of the solvent; this is an indication that the polar resonance structures of the excited molecules contain positive and negative groups which became solvated, i.e., the dipole vectors of the neighboring solvent molecules turn in a direction pointing towards the charged groups of the solute molecules. The relaxation time of the dipoles is long compared with the electronic motion (Franck-Condon principle), thus the influence of the static dielectric constant on the absorption is small; on the other hand the relaxation time is short compared with the lifetime of the excited state. Thus, fluorescence emission occurs practically only after the dipole cloud became oriented, that is, when the lowest energy state has been reached. Consequently, the fluorescence is appreciably shifted towards longer wave lengths in solvents with a high static dielectric constant. In a brief note, Bier & Ketelaar (188) pointed out that an emission spectrum of anthracene and phenanthrene complexed with symmetrical trinitrobenzene—although agreeing approximately with the position of the phosphorescence spectrum of the noncomplexed hydrocarbons—should not be ascribed to the singlet-triplet transitions. The rejection is based mainly on difficulties of understanding why the lifetime of the complexed state is 10^4 times shorter than that of the metastable state of the free aromatics. However, Moodie & Reid (189) showed that such a reduction of the lifetime by complexing has to be expected. The lifetime of the lowest triplet state in condensed hydrocarbons is abnormally long because the transition to the ground state violates two selection rules, one for intercombination and one imposed by symmetry relations. The formation of a complex causes distortion of the π orbitals (Mulliken) and consequently destroys the symmetry. This shortens the lifetime which now is comparable to that of intercombination transitions. The authors presented new measurements of singlet-triplet emission spectra of a number of carcinogenic hydrocarbons and of their complexes with 1,3,5-trinitrobenzene and found the similarities between corresponding spectra so great that the same type of electronic transition must be responsible for both. Another example in which complexing causes a considerable intensification of the lowest weak absorption band was described in some other connection by Suhrmann & Perkampus (190). The substance is 1,2,4-trimethyl-3-oxyphenazine and the complexing agents are alcohols. According to the reviewer's opinion, the explanation might be the same as that advanced by Moodie and Reid.

Triplet-triplet absorption spectra of some cyclic and heterocyclic aromatic hydrocarbons have been the object of an interesting and detailed study by Craig & Ross (191), thus extending previous work by McClure (192). Absorption from the lowest metastable triplet state was measured by means of a single-beam recording spectrophotometer in the range 7500 to 2650 Å. Triplet-triplet spectra are given, plotted on an arbitrary extinction scale, for naphthalene, fluorene and 7 larger hydrocarbons, for quinoline and isoquinoline and some larger mononitrogen heterocyclics, all in mixed rigid solvents. They show interesting features which, for lack of space, may not

be commented upon here, such as differences in intensity, amount of vibrational structure, distinction of one or two absorption systems. The transitions of the nine catacondensed hydrocarbons were suggested as being allowed. In contrast, no T—T spectra were found in benzene, hexamethylbenzene, diphenyl, diphenylamine, pyridine, or acridine, although they are expected and the position of an allowed in plane $^3E_g^+ - {}^3B_{1u}$ transition in benzene had been predicted. Reasons for the mentioned absences were discussed. Triplet-state lifetimes obtained from the decay rate of triplet-triplet absorption agree satisfactorily with those from the phosphorescence decay rate. It was observed that prolonged continuous irradiation caused noticeable diminution of triplet-triplet absorption, and photodecomposition was suggested as a possible explanation.

From a comparison of solution and crystal spectra of anthracene, Craig and collaborators (193) concluded that the two crystal absorptions in anthracene, a strong one at 2700 Å polarized along the *b* monoclinic axis and another to the shortwave side of 2300 Å strongly polarized in the *ac* plane, arise from the splitting of the single intense absorption in solution at 2500 Å considered as long axis polarized. The authors state that a simple calculation showed such a large "Davydov splitting" to be possible in an intense transition polarized along the long molecular axis. A similar assignment was extended to the polarized spectrum of tetracene crystals. To see whether this is the final explanation the full paper should be awaited. In order to test calculations made by Kuhn (194), Kuhn (195), and Dewar (196) of energy levels, and hence positions of electronic spectra for linear polyenes, a series of dimethylpolyenes ($CH_3 \cdot (CH=CH)_n \cdot CH_3$) have been prepared and their spectra taken (197). When $(\lambda_{n+1} - \lambda_n)$ was plotted against n for the longest wave length band, a curve with an inflection was obtained which could not be removed within estimated experimental errors, and could not be accounted for by one of the theoretical expressions. Since these equations were originally compared with spectral data of simple substances (butadiene) at one end and isoprenoid polyenes at the other because of missing information of simple polyenes, the new spectroscopic data will no doubt stimulate renewed theoretical efforts.

Using Platt's model and correlation scheme of the polyacenes and their spectra, Zanker (198) has given a similar scheme for the molecules and cations of pyridine, quinoline, and acridine. It was extended to a corresponding correlation of the spectra of mono- and diamino-substituted acridines. The spectra (absorption and, in some cases, also fluorescence) were studied with the substances in rigid glass solutions. Curves were obtained for the bases (neutral solution+alkali), the cations$^+$ (neutral salt solution) and the cations^{++} (acidic solution). Wave length shifts of the bands and their intensities were discussed and comparisons made of the spectral changes when going from an ether-alchohol solution to a strongly acidic solution (addition of H_2SO_4). This is an interesting paper which shows the wide applicability of Platt's method.—A paper by Russell (199) deals with the effect on the

spectra of phenylpyrimidines of substituents, in the 2- or the 4-position, or both, capable of conjugation with the chromophoric system. Weak absorption bands in the visible of *o*-benzoquinone and 1,2- and 1,4 naphthoquinone were recognized as $n-\pi$ transitions by Nagakura & Kuboyama (200) in analogy to similar bands of *p*-benzoquinone previously so assigned by McConnell (201). π-Electron densities of *o*- and *p*-benzoquinone were also given in (200). A beautiful piece of work has been done on the fluorescence spectrum of triphenylmethyl. Lewis, Lipkin & Magel (202) had observed that the fluorescence spectrum of triphenylmethyl in rigid glasses shows well-resolved structure. Weissman (203) enhanced the resolution of this spectrum by studying dilute solutions of triphenylhmethyl in crystalline triphenylamine at liquid nitrogen temperature and finally at 4°K. (liquid helium). In the latter case, an excellent line spectrum was observed which the author has good reason to ascribe to the emission from a vibrationless excited electronic state to the various vibrational levels of the ground state.

Mulliken's important theory of charge-transfer spectra was used by Murakami (204) to explain bond number and absorption spectra in the iodine-amylose complex. McConnell (205) raised the question whether I_4 is a self charge-transfer complex. Reid & Mulliken (206) made spectroscopic studies in the pyridine-iodine system and demonstrated the existence of the "outer" complex $Py \cdot I_2$ and the practical absence of the inner complex $(Py\ I)^+I^-$. By using solvents of different polarity, heat of formation, and other thermodynamic quantities of the outer complex were estimated. Ham (207) examined the effects of temperature and high pressures on the spectra of iodine solutions.

In concluding, a few remarks will be added on developments on some theoretical methods which pertain to all aromatic compounds. Great advances have been made last year in the theory of electronic spectra of conjugated systems. Since Parr and Ellison's review in this volume covers the subject adequately, it is sufficient to mention only a few important examples.

Generally speaking, two main approaches were followed: the electron gas model and the LCAO-MO theory. The valence-bond treatment is usually too involved to be practical, although the higher approximations of this method and the LCAO-MO method do merge. [For simplification and extension of the valence—bond method see McWeeny (208) and Wheland (209)]. The electron gas theory has been extended in two directions. First, the box model first proposed by Schmidt (210) was applied by Platt to a series of catacondensed systems (211). While the frequency predictions were poor, the electron densities were very good. The three-dimensional box model should not be confused with the one-dimensional network model proposed by Simpson, Bayliss and Kuhn. The branching conditions of the latter have been critically re-examined recently by Kuhn (212). A second development is the investigation of the role of interactions of electrons. Ingenious ways have been found by Araki & Araki (213) and by Araki & Murai (214) to take care of these, although a strictly Coulomb repulsion potential

leads to infinite interaction energy for the one-dimensional model.

More or less conventional free electron methods have been applied by Basu (215) and Nikitine and co-workers (216, 217) to complex conjugated systems. Coulson (218) applied the network model to metals which are usually treated by the 3-dimensional Sommerfeld model.

There is a close resemblance for conjugated systems between the one-dimensional free electron model and the LCAO-MO treatment. The similarity was stressed again by Griffith (219) and Ruedenberg (220). Moffitt (221) showed how Platt's perimeter electron gas model for catacondensed systems [a modification of which had been published by Nakajima (222)] can have its LCAO-MO analogue. Not only that, but the perturbations due to the introduction of cross links, which remove the degeneracies present in the unperturbed perimeter model, have a simple meaning. They give two types of perturbations: "odd" if the link connects a "starred" and an "unstarred" atom in the scheme of Longuet-Higgins (i.e., if there is an even number of atoms between the joints), and "even" otherwise. Substitution in this scheme is an even perturbation. It was shown that the two perturbations shift the unperturbed levels in entirely different ways. Regularities in catacondensed systems are explained satisfactorily, and besides, the difference between naphthalene and azulene becomes a consequence of the different nature of these two perturbations. The chief advantage of Moffitt's theory is its *Anschaulichkeit*, shared probably by few other models.

Striking agreement with experimental results has been achieved by the semiempirical theory of Pariser & Parr (223) and will continue to be so. The lowering of the value of the crucial $(pp|qq)$ integral from the theoretical value has been justified by Löwdin (5) to a certain extent as due to the "in out" effect.

Methods similar in contents to that of Pariser & Parr have been proposed by Pople (224, 225) and Goodman & Shull (226). Dewar & Longuet-Higgins (227) proposed a method aimed at accounting for regularities in the benzenoid hydrocarbons as Moffitt has done. They achieved this by removing the degeneracies inherent in Hückel's "naive" semiempirical theory through inclusion of the interelectronic repulsions.

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VIBRATION-ROTATION SPECTROSCOPY[1]

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Since the general background of vibration-rotation spectroscopy has quite recently been brought up to date in reviews of this series it seems possible to dispense with any general introduction to this subject. In this review it is proposed to indicate some present trends and to give a reasonably complete though not exhaustive account of recent contributions of general interest in the fields of infrared, microwave, and Raman spectroscopy. This account will largely be confined to the year 1954. which will be covered as far as certain practical limitations will permit. Though it will have been noted that the first and last of the fields mentioned were not reviewed in this series in the previous year, the greater part of that period is adequately covered by the comprehensive reviews on Infrared Spectroscopy by Gore (1), and on Raman Spectroscopy by Stamm (2).

Vibration Spectra

A continuing feature of infrared and Raman spectroscopy is the concentration of interest on halogen compounds, both organic and inorganic and, to a lesser extent, on compounds of boron and silicon. Very complete investigations have been made on a considerable number of these substances which, in many cases, have led to a virtually complete assignment of frequencies, and to calculations of thermodynamic properties which may be presumed to be reliable. Partial or complete normal coordinate treatments have been made in a number of cases. Investigations in 1954 contributing to our systematic knowledge of the types of compound mentioned are enumerated in Table I. Certain examples which have yielded structural information warrant further mention.

The rotational isomerism of 1,2-dichloroethane has been the subject of several papers by Nakagawa and co-workers (11, 12, 13) and further evidence has been given for the existence of a gauche form based on an assignment of bands assisted by a normal coordinate treatment. Isomerism of 1,1,2-trichloroethane was also investigated by Kuratani & Mizushima (14) and from the temperature dependence of intensities it was estimated that two forms differ in energy by about 3 kcal./mole in the gas phase. It was pointed out by Miller & Bauman (20) that although hexafluoro-2-butyne appears to follow D_{3d} selection rules this does not necessarily imply a staggered configuration but could equally well result from free rotation of the end groups. In disilane the structure of the ν_7 and ν_8 bands is taken by Gutow-

[1] The survey of the literature pertaining to this review was concluded in December, 1954.

TABLE I

VIBRATION SPECTRA

Halogen Substituted Methanes
CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, CF_4 (3); CF_3Cl, CF_3Br, CF_2I (4, 5); $C^{13}H_3I$ (6); normal coordinate treatments (4, 7, 8).
Halogen Substituted Ethanes
ethyl chloride, 1,1-dichloroethane (9, 10); 1,2-dichloroethane (assignments, force constants, rotational isomerism) (11, 12, 13); 1,1,1-trichloroethane, 1,1,1,2-tetrachloroethane, pentachloro- and hexchloroethane (10); 1,1,2-trichloroethane (rotational isomerism) (14).
Halogen Substituted Ethylenes
ClHCCHCl (*cis* and *trans*) (15); C_2F_3H, C_2F_2D (16); C_2F_3Cl (17); C_2Cl_4, C_2F_4 (18); C_2F_3Br (19).
hexafluoro-2-butyne (20)
Other Halogen and Interhalogen Compounds
ReF_6 (21); $(PNCl_2)_3$, $(PNCl_2)_4$ (22); $POCl_3$, POF_3, $PSCl_3$, PSF_3 (normal coordinate treatment) (23); $SOCl_2$, SO_2Cl_2 (24); BrCl (25); BrF_3, BrF_5 (26); $HF \cdot ClF_3$ (27).
Boron Compounds
B_5H_9, B_5D_9 (28); $(CH_3)_2NB_2H_5$, $(CD_3)_2NB_2D_5$ (29)
Silicon Compounds
Si_2H_6 (30); $Si_2(CH_3)_6$ and other substituted silanes (31)

sky & Stejskal (30) to indicate a barrier to rotation which is at least comparable to that in ethane.

From the selection rules which seem to be applicable, the RF_6 molecule appears to have the symmetrical octahedral structure [Gaunt (21)]. The trimer of $PNCl_2$ seems to follow D_{3h} selection rules but no definitive decision could be made between point groups D_{4h} and D_{2d} for the tetramer [Daasch (22)]. The interesting complex of HF and ClF_3 was studied spectroscopically and ΔH of association estimated to be -3.9 kcal./mole. No hydrogen bond appears to be involved. [Pensler & Smith (27)]. Some evidence was found for a similar complex between HF and BrF_3 [Haendler *et al.* (26)].

Mention should be made of several investigations with the purpose of elucidating the structure of interesting organic molecules. These include formamide (32, 33), methyl-substituted hydrazines (34), and cyclopropane (35). Some minor reassignments have been made in the spectrum of ketene (36). Several observations have been made on the interesting substance *S*-triazine (37, 38, 39) of which the existence was only recently demonstrated

by Grundmann & Kreutzberger (40). It is a matter for congratulation that the spectrum of carbon suboxide has at last been brought into compatibility with a linear structure for this molecule [Long *et al.* (41)]. An interesting attempt has been made by Lord & Walker (42) to decide between proposed alternative structures for two dimers of cyclooctatetraene on a statistical basis. Since the spectra are too complicated for a detailed analysis to be made at present, a comparison was made of the number of bands observed in a given spectral region with the number which might be expected to occur with each structure. The results of this treatment were rather inconclusive.

Group and characteristic frequencies.—An excellent survey of the present status in this field is given in the recent book by Bellamy (43) which will be very useful both to those concerned with analytical problems and to those engaged in structure determinations. It will be noted that the section on halogen compounds is relatively incomplete, since the author considers that the spectra of these are of comparatively little interest from the analytical standpoint. In a recent note he has, however, pointed out useful regularities in the spectra of fluorinated hydrocarbons (44). Other references to the extensive work on halogen compounds have been given in this survey, and numerous recent additions have been made to the American Petroleum Institute *Catalog of Infrared Spectral Data* (45).

Knowledge is now reasonably complete regarding the more striking group frequencies associated with vibrations highly localized in specific groups of a molecule, and relatively insensitive to environment. On the other hand, knowledge continues to accumulate either regarding less obvious regularities characteristic of structural features, or relating to the effects of environment and other factors on group frequencies, which may be useful in structure determinations. It is beyond the scope of this review to enumerate all recent contributions of this character, but a few systematic studies relating to the second of these categories may be mentioned.

Previous studies on the effect of environment on the carbonyl frequency have been extended to over 100 ketones and quinones by Fuson *et al.* (46). Goulden (47) has observed that within a particular class of compound the OH frequency of carboxylic acids and of phenols varies linearly with pK_a. Leonard & Gash (48) have shown that α, β-unsaturated amines can be distinguished by the considerable increase in C=C frequency which occurs on salt formation. Corbridge & Lowe (49) have made systematic studies on a large number of salts of phosphorus oxy-acids and point out regularities of analytical interest.

With certain notable exceptions the region lying roughly between the visible and 2.8 μ has until now not been used very extensively either in structural determinations or for analytical purposes, and its possibilities have consequently not been fully explored. With the appearance of several commercial spectrometers giving moderate to high dispersion in this range, new applications may be anticipated. Some special applications have been discussed by Kaye (50).

Vibration spectra of adsorbed substances.—A field which has been little exploited but has interesting possibilities is the study of adsorbed materials by the techniques of infrared spectroscopy. French *et al.* (51) have used the potassium bromide matrix method to study materials adsorbed on clays. Eischens and co-workers (52) have investigated the condition of carbon monoxide adsorbed on different metals which, in finely divided form, were supported in matrices of silica particles. Large decreases in the CO-stretching frequency result from the adsorption and, in certain cases, the shifted frequencies suggest that carbon monoxide molecules are attached to the metal in two different ways. Ammonia adsorbed on cracking catalysts was found to exhibit both NH_3 and NH_4^+ bands, with the former predominant. These results were taken to indicate that the acid centers of the catalyst are at least for the greater part of the Lewis type (53).

Normal coordinates and potential functions.—The analysis of a vibration spectrum is frequently attended by a dynamical treatment of the molecule in question, known as a normal coordinate analysis. This is, in general, only practical to the approximation that the vibrations are regarded as infinitesimal, so that terms higher than second-order can be neglected in the potential function. When information on similar molecules is available, so that approximate values for the major potential constants may be "transferred," such a treatment may be very useful in the identification of fundamentals, and even in supplying approximate values for certain frequencies which may not be observed directly, but are required for the calculation of thermodynamic properties. In very few cases, however, are sufficient data available for the direct determination of a unique potential function which has real validity through all second-order terms, and one has usually been content with the criteria for a satisfactory function that the fundamental frequencies be reproduced within small limits, and that the potential constants be reasonable. In view of our limited knowledge regarding interaction constants, these standards may be rather inadequate as more stringent demands are put on the potential function. In a number of applications which may be expected to be of increasing interest, it is necessary that the normal modes of vibration be correctly reproduced. These include the quantitative study of the intensities of vibration rotation bands, and the more refined interpretation of electron diffraction in gases and x-ray diffraction in crystals. In the latter fields the development of experimental techniques will make it more and more necessary to take the thermal motions of atoms into account. It seems very probable that electron diffraction may shortly be able to provide information regarding normal modes which may be very helpful in restricting the possible potential functions.

Another difficulty should be mentioned. Only in extremely few cases is the complete set of convergence constants known which permit one to calculate zero amplitude frequencies from the observed fundamentals, though a correction is sometimes made for the hydrogen frequencies alone, as, for example, in the treatment of ethylene by Crawford *et al.* (54). This practise has

been deprecated by Manneback & Rahman (55). The possible effect of neglect of convergence on the estimation of normal modes is perhaps not completely explored, but it should also be mentioned that it seems likely, even for certain rather low frequencies, that the zero amplitude modes will not be quite adequate in the quantitative discussion of intensities and in some other applications.

Fortunately, in cases where rotational structure is resolvable, additional information can be obtained from centrifugal distortion and from Coriolis coupling constants which may put strict limitations on the potential constants. A combined use of vibrational data obtained from isotopic molecules and of microwave rotational data has led to precise potential constants for SO_2, though with neglect of the effects of anharmonicity [Polo & Wilson (56); Kivelson (57)]. It is interesting that the bond-bond interaction constant, though positive, was found to be only 0.3 per cent of the bond constant, which at first sight seems very small for a molecule of this type. Potential constants have also been obtained for ClO_2 from a combination of various data [Ward (58)]. Both interaction constants were found to be negative, which is contrary to the prediction of theory.

A systematic treatment of centrifugal distortion in polyatomic molecules has recently been given by Kivelson & Wilson (59), and the relation of Coriolis coupling constants to potential constants has been discussed by Polo & Hawkins (60).

The calculation of the shapes and magnitudes of the potential barriers which prevent free rotation about single bonds has been discussed by Luft (61) who has also considered the particular case of the halogen substituted ethanes (62). He points out that a simple additivity rule holds fairly well for these compounds. From a systematic consideration of the existing data he believes it is possible to remove some ambiguities in vibrational assignments and that the barrier previously assigned to $F_3C\text{-}CHCl_2$ was somewhat too high.

It has been a common desire to classify fundamental frequencies by such descriptive names as "C—H valence," or "C—H bending" modes. If this is attempted on the basis of amplitudes some ambiguities may result, which are sometimes resolved if the distribution of potential energy is taken as a criterion for the type of vibration. Taylor (63) has pointed out that even this device may be inadequate and misleading.

A number of interesting empirical relations between potential constants, internuclear distances and other data have recently been pointed out. Some years ago Sutherland (64) showed that a general relation between dissociation energy, equilibrium internuclear distance and force constant, held fairly well for the ground states of diatomic molecules. Frost & Muslin (65) find that a similar relationship extends to $(\partial^3 V/\partial r^3)_{r=r_e}$, but apparently much less well to the fourth derivative, though the experimental data are indeed less reliable. Aroeste (66) has found a curious relationship between infrared intensities and other parameters which obviously cannot be quite general.

For the few diatomic molecules for which data are available the derivative of the dipole moment with distance seems to be proportional to the dissociation energy, and inversely proportional to the square of the internuclear distance. Mitra (67) finds a simple relation between the force constants of diatomic hydrides and the number of electrons in the outer shell of the element in question.

Margoshes *et al.* (68) have found that the carbonyl frequency correlates quite well with C=O bond distance in a number of compounds, in spite of the fact that the interaction between the carbonyl vibration and other molecular modes must be rather different in the various compounds. Since the frequency shifts about 30 $cm.^{-1}$ per hundredth Angstrom in bond length, very small differences in the latter should be detectable if all factors could be taken into account.

Intensities in vibration-rotation spectra.—Considerable progress will have to be made before theory is in a position to make reliable and accurate predictions of bond moments and polarizabilities, and of the derivatives of these quantities with respect to internuclear distances, but empirical knowledge obtained from the accurate measurement of intensities in both infrared and Raman spectra continues to accumulate. Among the very recent investigations should be mentioned the infrared measurements on GF_4, SiF_4, and SF_6 by Schatz & Hornig (69), on NO, HCl, and HBr by Penner & Weber (70), and on COS by Wingfield & Straley (71).

The relation of the intensities of fundamental and overtone vibration bands of diatomic molecules to the derivatives of the dipole moment with respect to distance and to the anharmonicity of the potential function has been the subject of many theoretical papers [for references see (72)]. In some of these treatments perturbed harmonic oscillator wave functions have been used, in others the Morse functions, though in the latter case it appears impracticable to include terms higher than quadratic in the dipole moment expansion. Herman & Shuler (72) have extended the former perturbation treatment, but they conclude that the use of the Morse functions is superior in spite of the restriction mentioned. The reason is that in the range of internuclear distance of interest the potential function departs markedly from the harmonic oscillator approximation while the dipole moment exhibits little deviation from linearity. The interpretation of Raman intensity data in terms of polarizability functions characteristic of individual bonds should be facilitated by a matrix method which Long (73) has set up and which has been applied to the case of neopentane (74).

The effect of the difference in asymmetry in ground and excited states upon relative intensities of vibration-rotation lines of an asymmetric rotor has been investigated by Allen (75). In certain light molecules this difference may be rather large and may result in anomalies in intensity which might be a useful aid in the analysis of vibration rotation bands.

Fahrenfort & Ketelaar (76) have recently observed a very interesting phenomenon which appears to be new though its possibility had been pre-

viously discussed (77). In high pressure mixtures of CO_2 and either N_2, O_2, or H_2, gases which have no (dipole) vibration-rotation spectrum, absorptions have been observed which are attributed to simultaneous vibrational transitions in CO_2 and N_2, O_2 or H_2 molecules, as the case may be. The frequencies of the centers of the bands observed differed by less than 10 cm.$^{-1}$ from the sum of the frequency of an active CO_2 fundamental and the vibration frequency of the other gas. The question suggests itself as to whether this type of process does not occur frequently in solutions.[2] The conditions for its observation will, however, usually not be very favorable.

Investigations of Rotational Structure

The availability of high quality diffraction gratings has considerably extended the capacity of both infrared and Raman spectroscopy. With the use of efficient light sources, Stoicheff & Møller (78, 79) have been able to observe the Raman spectra of gases at very moderate pressures and to obtain a resolution of about 10^6 at λ4358. It has consequently become possible to make direct measurements of the rotational constants of quite heavy, nonpolar gases. Investigations have been made on C_6H_6, D_6H_6, and $(CN)_2$ and accurate values have been obtained for the parameters of benzene, namely: $r_{CC} = 1.397_3 \pm 0.001$ Å, $r_{CH} = 1.084 \pm 0.006$ Å.

In the near infrared the use of sensitive photoconductive detectors has permitted a resolution of about 1.5×10^6 to be attained (80), and the consequent high resolution in frequency makes it possible to study details in structure which were formerly inaccessible. There are some limitations to the utility of this resolving power which in principle might be removed, but present practical difficulties. The overlapping by "hot" bands is often inconvenient, and the high pressures required for the observation of weak bands may cause excessive line broadening.

Among high resolution investigations in the near infrared should be mentioned the studies of *l*-type doubling in C_2H_2 and HCN by Wiggins *et al.* (80) which have shown that assumptions usually made in the analysis of $\pi \rightarrow \pi$ bands are not justified and that more constants are required for an adequate description. Methyl fluoride has been reinvestigated by Pickworth & Thompson (81, 82) who achieved the most complete analysis of a perpendicular type band which has so far been possible for a symmetrical top molecule. In a very thoroughgoing investigation Allen & Plyler (83, 84) have resolved and analyzed the structure in badly overlapping H_2S bands in both 5100 cm.$^{-1}$ and 6290 cm.$^{-1}$ regions, which present some features of interest. In both cases a band of otherwise vanishing intensity is activated by Coriolis interaction between two practically coincident upper vibrational levels of different symmetries. The (0, 2, 1) band has been located at 4939.23 cm.$^{-1}$ and this observation, together with other data, permits a new and more accurate

[2] An example of this sort has indeed been reported. See Ketelaar, J. A. A., and Hooge, F. N., *J. Chem. Phys.*, **23**, 749 (1955)

estimate to be made of the origin of the curious, asymmetric, (0, 0, 1) fundamental, which is now believed to lie at 2628 cm.$^{-1}$. In the temperature emission spectrum of H_2O about 1000 lines have been observed. The spectrum has been analyzed and several new rotational levels observed [Benedict, Bass & Plyler (85)]. Douglas & Møller (86) have obtained new data on isotopic molecules of N_2O. Though the extrapolation of the rotational constants to the vibrationless state presents some problems because of inconvenient Fermi resonance, the equilibrium internuclear distances have been obtained with reasonable accuracy and were found to be: $r_{NN} = 1.126$ Å and $r_{NO} = 1.186$ Å with estimated errors of about 0.002 Å. An independent investigation of the change in rotational constants with vibrational state in N_2O has been made by Christensen & Thompson (87).

In other investigations extending into the intermediate infrared, rotational structure has been investigated in at least a portion of the observed bands and new or more precise molecular parameters determined. A study was made on HDCO by Davidson *et al.* (88) in an attempt to locate the hydrogen atoms more accurately. In former investigations on H_2CO and D_2CO the analysis of the perpendicular bands was prevented or hampered by the large Coriolis interactions or by overlapping. In the recent work disturbances were also present, and although values for the large rotational constant obtained from infrared and Raman spectra are in agreement, the probable errors are rather large and the molecular parameters are still not located within close limits. A C—H distance not far from 1.07 Å seems probable.

The analysis of the vibration rotation bands of SiH_4 and of GeH_4 is not a simple procedure and some uncertainty has been attached to the internuclear distances found for these gases. Wilson and co-workers have taken a direct approach and have analyzed parallel bands of SiH_3D (89) and of GeH_3D and $GeHD_3$ (90) from which it was found that in the lowest vibrational state the silicon hydrogen distance is 1.477 ± 0.003 Å and the germanium hydrogen distance is 1.529 ± 0.003 Å in GeH_3D and 1.525 ± 0.005 Å in GeH_3D. These distances are appreciably larger than those obtained from the former infrared measurements, and are more nearly in agreement with the distances found in halogen substituted silane and germane by microwave measurements. Rotational constants in good agreement with microwave values have been obtained for the perpendicular infrared bands of H_3GeCl by Lord & Steese (91) but the spectrum of the deuterated molecule was not resolved. A parallel band has been resolved by Nielsen (92) in the spectra of both $B^{10}F_3$ and $B^{11}F_3$. The rotational constants were identical for both molecules and the B—F distance was found to be 1.295_1 Å.

Reinvestigations of deutero-methyl acetylene (93) and of dimethylacetylene (94) with high dispersion have been made by Thompson and coworkers, and the virtual absence of any barrier to internal rotation in the latter molecule appears to be confirmed. Other high dispersion investigations include those on $(CN)_2$ and diacetylene (95), on OCS (96), and on $C^{14}O_2$ (97).

Spectra of Intermediate and Large Molecules

Certain of the most striking regularities in the infrared spectra of polymethylene chains were pointed out fifty years ago in the early systematic investigations of Coblentz (98), but only in the last ten years have the extensive investigations been possible which have led to an approximate understanding of these spectra, and to the assignment of methylene bending, wagging, twisting, and rocking motions to more or less definite spectral ranges. [For references to the numerous contributions to this field see (99)]. Considerable progress has been made very recently in the more detailed interpretation and in the systematization of the polymethylene spectra.

Recent experimental investigations on $X(CH_2)_nY$ molecules include the infrared observations of Sheppard *et al.* on odd-numbered normal paraffins up to *n*-nonadecane (99) and on *n*-alkyl bromides up to *n*-bromodecane (100); of Günthard *et al.* on methyl esters of dicarboxylic acids with *n* even and lying between 14 and 32 (101, 102), and on a few diketones and ketoesters (102); and of Hidalgo on some diphenyl paraffins (103). It has been shown that in the crystalline state the normal paraffins assume a planar zig-zag configuration, which appears to be true also of at least some derivatives. By studying these substances in the solid state the complications of rotational isomerism are removed and the interpretation of the spectra greatly facilitated.

Brown, Sheppard & Simpson (99) have succeeded in ordering a large number of polymethylene frequencies into four series by qualitative considerations regarding the manner in which a frequency associated with a methylene mode may be expected to split repeatedly with increasing chain length. By following these series down to low molecular weight hydrocarbons where the molecular mode responsible can be identified, it has been possible to establish the general character of the motions responsible for each series. Two series are particularly striking. One, attributed to methylene rocking motions has its origin at 748 $cm.^{-1}$ in propane and develops systematically into a very asymmetric pattern covering the range 700 to 1000 $cm.^{-1}$ in higher hydrocarbons. A somewhat similar series due to methylene wags, covers the range 1200 to 1380 $cm.^{-1}$ and is particularly striking in the bromides, the esters, and the fatty acids (104). Less definite patterns are attributed to methylene twists in the range 1170 to 1300 $cm.^{-1}$ and to C—C stretch covering the region 850 to 1050 $cm.^{-1}$.

Extensive normal coordinate treatments have recently been made on polymethylene chains by Primas & Gunthard (102, 105, 106). As one might expect, the predicted frequencies do not agree in detail with observation, but the frequency ranges mentioned are well supported and in particular the asymmetric pattern of the CH_2 rocking modes is well accounted for.

The selection rules for the skeletal vibrations of long chain polymers in the crystalline state have been discussed by Liang, Sutherland & Krimm (107) who point out that in the infinite chain only those skeletal modes will be active in which all atoms move in phase. The more complicated situation

in helical molecules has been treated by Higgs (108). A vibrational analysis of polypeptide chains has been reported (109), but no details have been published.

In the field of proteins, polypeptides, and related substances a number of scattered observations relate to the probable molecular configuration in solution. As has been recently shown, observations in the 6μ region are practicable if heavy water is used as solvent (110, 111). Lenormant & Blout (112) have taken advantage of this to follow the denaturation of several proteins by shift of the amide band near 1640 cm.$^{-1}$. They also observed similar changes in the spectrum of DNA resulting from the action of desoxyribonuclease, from heating, or from increase of pH (113). Only the very qualitative interpretation that changes in molecular configuration occur is now possible, since the relation between the peptide frequencies and chain configuration is not well understood. Empirical use of the 1640 cm.$^{-1}$ band has, however, been made by Doty *et al.* to investigate the condition of the poly-γ-benzyl-L-glutamate in various solvents (114). The assumption that a high frequency in this band corresponds to a well organized coiled structure, such as an α-helix, and a low frequency to a more outstretched, but less rigid structure appears to be supported by viscosity measurements.

Though the qualitative use of polarized infrared spectra has been useful in structural investigations of polypeptides, the quantitative application is hampered by the present lack of criteria for the degree of crystallinity and of orientation such as have been developed for other high polymers, as for example, polyethylene (120). In this substance the splitting of bands at 13.8 μ and 7.6 μ appears to offer a measure of crystallinity. The splitting of the 13.8 μ band in oriented material has been attributed by Krimm (121) and by Keller & Sandeman (122) to interactions with neighboring molecules. The 7.6 μ band, on the contrary, splits in the molten state, which Novak (123) attributes to rotational isomerism. Quynn & Steele (124) have made some interesting observations on changes in dichroism in the 3075 cm.$^{-1}$ amide band in nylon, which result from reorientation by drawing. The origin of this band has been the subject of considerable discussion in connection with amides and polypeptides.

Slight differences in frequency of the 1640 cm.$^{-1}$ band in L and *meso* forms of synthetic polypeptides were found by Elliott (115), but no systematic variations were found in the peptide band near 1560 cm.$^{-1}$.

Though spectroscopic studies have not as yet led to the elucidation of any protein structure they may be helpful in deciding between alternative structures and in discarding models which may at first seem plausible. Models so far proposed for collagen have been in conflict with infrared observations both from the standpoint of frequencies and of polarization data. The structure recently proposed by Crick (116) involves eight-membered rings closed by two hydrogen bonds and lying perpendicular to the fiber axis. The abnormally low N-H frequency (117) and the parallel dichroism in the out of plane N-H bending frequency (118) predicted for this configuration

are not in conformity with the observed spectrum. Of interest in connection with collagen, which has a relatively large proline content, is the recent observation by Berger *et al.* (119) that the 1540 cm.$^{-1}$ peptide band is absent from the spectrum of poly-L-proline.

Microwave Spectra of Gases

In Table II appearing in this section there is given what is hoped to be a reasonably complete enumeration of microwave investigations reported in 1954 which have contributed data of structural interest. For those unfamiliar with the theoretical basis for the interpretation of microwave spectra and with the fundamental techniques of measurement, the recent book by Strandberg (125) will be found useful.

A recent development in microwave spectroscopy which is of particular interest because of the fund of data which it has made available, is the high temperature investigation of involatile substances (126, 127). Honig *et al.* (128) have made a very complete investigation of 15 of the 20 alkali halides, and the data which they have obtained regarding the relation between bond character, internuclear distance, dipole moment, etc., is of both practical and theoretical value.

Investigations leading to complete sets of molecular parameters, as well as to other constants, have been made on several polyatomic molecules. Of considerable interest are the fluorides of perrhenic acid and of permanganic acid, recently prepared in the pure state by Engelbrecht & Grosse (130), since volatile compounds of manganese and rhenium suitable for electron diffraction or microwave observations are rare. Both MnO_3F and ReO_3Cl were shown by Javan & Engelbrecht (131) to be symmetrical tops and in the former manganese was found to form nearly tetrahedral bonds. In SOF_2 Ferguson (132) found an S—O distance of 1.412 Å, considerably longer than the abnormally short distance of 1.370 Å reported for sulfuryl fluoride by Fristrom (133). Gordy & Sheridan (134) demonstrated the linear arrangement of heavy atoms in CH_3HgCl and CH_3HgBr and from the quadrupole coupling constants estimated the percentage of ionic character of the mercury halogen bond and placed mercury at 1.7–1.8 in the electronegativity scale. The molecules of stable pentaborane were shown by Hrostowski & Myers (135) to be pyramidal, probably with C_{4v} symmetry. Hardy & Silvey (136) observed seven stable isotopes in the spectrum of TeCS, measured the mass ratios and compared them with mass spectrometer data. Heath *et al.* (137) evaluated the molecular parameters of trifluorosilane.

Rotational constants were measured for a number of heavier molecules for which the data was insufficient to deduce parameters but for which structural information of interest was obtained. The nonplanarity of the carbon ring in cyclopentanone was confirmed by Erlandsson (138), whereas vinyl carbonate was shown to be planar by Slayton *et al.* (139). Rotational constants and quadrupole coupling constants were obtained for vinyl cyanide by Wilcox *et al.* (140) and vinyl iodide, which is of interest because of some

TABLE II

MICROWAVE INVESTIGATIONS

Molecule	Data obtained*	Reference
O_2	effect of centrifugal distortion	(168)
	Zeeman effect and line breadths	(176)
OD	Λ-type doubling parameters	(177)
NO	Λ-type doubling parameters and hfs	(178)
$N^{14}O^{16}$	$B_o = 1.69510$ cm.$^{-1}$ $r_o = 1.1539$	(179)
KCl, NaCl	Stark effect	(129)
Alkali halides	very complete data on 15 alkali halides	(128)
H_2O	absolute intensities	(174)
	$2_{2,0} \rightarrow 3_{1,3}$ line at 183311.30 Mc.	(162)
H_2O, D_2O, HDO	centrifugal distortion	(180)
HDO	$A = 7.0396$, $B = 2.7360$, $C = 1.9186$, $\kappa = -0.6841$	(180)
HCN	Variation of l-type doubling constant	(181)
	$q(\text{Mc}) = 224.471 - 0.002613\ J(J+1)$	
	direct l-doublet transition $J = 3$, $v_2 = 1$	(182)
DCN	$(eqQ)_D \approx \pm 145 \pm 60$ kc.	(183)
DBr^{79}	$(eqQ)_{Br} = 533$ Mc, $B_o = 1286_{15}$, $r_e = 1.414_{40}$	(165)
DBr^{81}	$(eqQ)_{Br} = 455$ Mc, $B_o = 1285_{28}$, $r_e = 1.414_{39}$	
HDS^{33}	$Q_{S^{33}} = (-0.064 \pm 0.01) \times 10^{-24}$ cm.^{2}	
$S^{33}O_2$	estimated quadrupole moments for	(184)
$CH_3S^{33}H$	O^{17} and Se^{79}	
OCS^{32}	$D_J = 1.310 \pm 0.010$ kc.	(162)
OCS^{33}	$J = 1 \rightarrow 2$, $v_3 = 1$ at 0.85 Mc.	(185)
OCS^{35}	$\mu_{S^{35}} = 1.00 \pm 0.04$ nm.	(186)
$OCSe^{75}$	$I_{Se} = 5/2$, $(eqQ)_{Se} = 946$ Mc., $Q_{Se} = 0.9 \times 10^{-24}$ cm.^{2}	(187)
TeCS	$r_{TeC} = 1.904$, $r_{CS} = 1.557$, $\mu = 0.172$ D	(136)
	mass ratios for Te isotopes	
O_3	reexamination	(188)
H_2O_2, D_2O_2, HDO_2	barrier ~ 113 cm.$^{-1}$, $\mu = 2.26$ D	(158)
$N^{14}H_3$	hfs, change in eqQ by centrifugal distortion	(189, 190)
PH_3	$B_o = 133478.3$, $r_{PH} = 1.4206$	(191)
PD_3	$B_o = 69470.41$, $r_{DH} = 1.4166$	
AsH_3	$B = 5747.6$, $(eqQ)_{As^{75}} = -165.6$ Mc.	(192)
DCCCl	$(eqQ)_D = +175 \pm 20$ kc.	(183)
NF_3	$\mu = 0.235 \pm 0.007$ D	(193)
$AsCl_3$	$(eqQ)_{As} = -173 \pm 20$ Mc.	
$SbCl_3$	$r_{SbCl} = 2.325 \pm 0.005$, $<\text{ClSbCl} = 99.5 \pm 1.5°$	
HCOOH	$B = 12055.9$ $C = 10415.3$	(145)
HCOOD	11762.4 9970.3	
CH_3F^{19}	$B_o = 25536.11$, $D_{JJ} = 59.3$ kc., $D_{JK} = 445$ kc.	(164)
CH_3CL^{35}	$= 13292.86$ $= 18.1$ kc. $= 198$ kc.	
CH_3Br^{79}	$= 9568.2$ $= 9.9$ kc. $= 128.3$ kc.	

TABLE II (Continued)

Molecule	Data obtained*	Reference
CH_3I	quadrupole spectrum	(194)
CH_3NH_2	internal rotation barrier$\sim$1.8 kcal. mole^{-1}	(156, 157)
CH_3NO_2	internal rotation barrier$\sim$6.00 cal. mole^{-1}	(154)
CH_3CH_2F	rotational constants, barrier height	(195)
CH_3CHF_2	$A=9491.95$, $B=8962.65$, $C=5170.43$, $\kappa=0.75504$ barrier $=(1.3\pm0.2)\times10^3$ cm.$^{-1}$	(196)
vinyl cyanide	$A=49076.2$, $B=4971.33$, $C=4514.05$ $\chi_{aa}=-3.0$ mc., $\mu=3.89$ D	(140)
vinyl iodide	$(B+C)=6325.41$, $(B-C)=192.03$, $\kappa=-0.9921554$	(141, 142)
vinylene carbonate	$A=9346.79$, $B=4188.46$, $C=2891.54$ $\kappa=-0.59818$, $\mu=4.51$ D	(139)
methyl-cyanoacetylene	$B_o=2065.73$, $D_J\sim0.1$ kc. $D_{JK}=19.8$ kc., $(eqQ)_{N^{14}}=-4.4$ Mc.	(143)
cyclopentanone	$A=6618.8$, $B=3350.8$, $C=2409.9$	(138)
C_6H_5CN	$A=5654$, $B=1546$, $C=1214.5$, $\kappa=-0.8505$	(149)
C_6H_5F	reexamination	(148)
pyridine	———	(146, 147)
F_3SiD / F_3SiH	$r_{SiH}=1.455$, $r_{SiF}=1.565$, $\angle FSiF=108°17'$	(137)
CH_3SiH_3	rotation barrier$\sim$1.6 kcal./mole	(152)
$(CH_3)_3SiF$	$B_o=3411.00$ ($r_{SiF}\sim1.55$)	(151)
CH_3HgCl / CH_3HgBr	$r_{CH_3}=2.061$, $r_{HgCl}=2.282$ $\angle CHgCl=180°$ / $r_{CH_3}=2.074$, $r_{HgBr}=2.406$ $\angle CHgBr=180°$	(134)
SOF_2	$r_{SO}=1.412$, $r_{SF}=1.585$, $\angle FSF=92°49'$ $\angle OSF=106°49'$	(132)
B_5H_9, B_5D_9	parameters, dipole moments, etc.	(135)
ReO_3F	$B_o=3566.751$, $(eqQ)_{Re}=-53$ Mc.	(197)
ReO_3Cl / MnO_3F	$Q_{Re^{187}}/Q_{Re^{185}}=1.067$, $(eqQ)_{Re^{187}}=253$ Mc. $Q_{Re^{187}}=0.55\times10^{-24}$ cm.^{2} $r_{MnO}=1.586$, $r_{MnF}=1.724$, $\angle OMnF=108°27'$ $(eqQ)_{Mn^{55}}=16.8$ Mc., $Q_{Mn^{55}}=0.55\times10^{-24}$ cm.^{2}	(131)

* Internuclear distances are given in Angstrom units, and unless otherwise specified rotational constants are given in Mc.

double bond character in the carbon halogen bond has been investigated by Cornwell & Poynter (141) and Morgan & Goldstein (142). Methyl cyanoacetylene was shown by Sheridan & Thomas (143) to have the linear cyanide structure. The combined results of infrared and microwave measurements have not as yet led to a unique and wholly reliable set of parameters for formic acid, and there appears to be an appreciable discrepancy between the infrared data of Williams (144) and the microwave measurements of Trambarulo & Moser (145). The interpretation of the pyridine spectrum has been discussed by Bak *et al.* (146) and new measurements have been made by Mc-

Culloh & Pollnow on this substance (147) and on fluorobenzene (148). Rotational constants have been obtained for benzonitrile by Erlandsson (149); for ethyl chloride by Wagner & Dailey (150) and for $(CH_3)_3SiF$ by Gunton *et al.* (151).

Several recent investigations deal with the spectra of molecules with hindered internal rotation and with attempts at a detailed interpretation. A special case is the symmetrical top such as methyl silane, in which the moments of inertia are independent of the internal rotation, and the rotational constants are affected only in higher order through interaction between internal rotation and other vibrational modes. The approximate theory for this case has been presented by Kivelson (152) and empirical constants obtained with which a number of lines in the methyl silane spectrum are very satisfactorily fitted. These include a potential barrier against internal rotation of about 1600 cal. $mole^{-1}$, which is significantly less than the 2800 cal. $mole^{-1}$ found in ethane by Hansen & Dennison (153) as should be expected. The unsymmetrical rotor, nitromethane has been treated by Tannenbaum *et al.* (154), using the methods of Burchard & Dennison (155). Evidence was found for the existence of a sixfold potential barrier which is, however, extraordinarily small, and is estimated to be 6.00 ± 0.03 cal. $mole^{-1}$. Further work has been done by Shimoda *et al.* (156) and by Lide (157) on methyl amine which presents the additional complication of inversion doubling. Lide fitted the mean frequencies of several inversion doublets by an approximate treatment in which the potential barrier to rotation was taken to be 1800 cal. $mole^{-1}$, but a more complete treatment is to be desired. An approximate treatment of the spectrum of hydrogen peroxide has been attempted by Massey & Bianco (158) using the simplest sinusoidal potential function with two equal maxima and barrier height of about 320 cal. $mole^{-1}$. It is difficult to reconcile this barrier with the reported torsional frequency of hydrogen peroxide at about 500 $cm.^{-1}$ (159). Precise theoretical calculations are difficult but two estimates have placed a lower limit of about 6 kcal. $mole^{-1}$ on the barrier height (160, 161). Further work on this interesting molecule seems to be indicated.

Several recent measurements have been made in the millimeter and submillimeter wave region. Measurements by Gordy and co-workers (162, 163, 164) on higher rotation lines of OCS, the methyl halides, and on water vapor have led to accurate values of the centrifugal stretching constants. Observations were made on DBr (165) which has the smallest moment of inertia of any molecule so far measured.

A number of recent investigations relate to intensities and line shapes. Saturation has been observed by Bird (166) in the rotation spectrum of methyl chloride, the only previous example being in the ammonia inversion spectrum. Observations have been made on two molecules which do not have permanent dipole moments, namely on CO_2 at high pressures by Birnbaum *et al.* (167) and on O_2 by Mizushima & Hill (168) and the origin of their spectra has been discussed. Further investigations have been made on pres-

sure broadening and the effect of temperature. Liuima *et al.* (169) and Feeny *et al.* (170) have made measurements on OCS, and Krishnaji & Swarup (171) and Birnbaum & Maryott (172) on ammonia. Artman & Gordon (173) have attempted to obtain reliable data on line widths and intensities in oxygen and in mixtures of oxygen and nitrogen. Rogers (174) has reduced the apparent discrepancy between predicted and measured intensities in water vapor, but variations in collision half width from line to line appear to be real.

With the precision of measurement and resolving power now available, microwave spectroscopy offers a means of determining isotopic mass ratios which competes in accuracy with other methods. Where the element in question is obtainable in a diatomic molecule only a relatively straightforward comparison of the rotational constants of appropriate isotopic molecules is involved, though several corrections may need to be applied. The rotational constants must be corrected to the vibrationless state, and allowance may be necessary for contributions to the effective rotational constants from the L-uncoupling of electrons which results from the molecular rotation. At present the second correction is significant only for lighter molecules which are observed in states of high rotational velocity, but does probably contribute the chief uncertainty in the mass ratio for deuterium and tritium. Finally, uncertainties may arise from electronic distribution. In the extreme case of a completely ionic molecule the effective masses would be those of the ions rather than those of neutral atoms. Mass ratios probably accurate to a few parts per million have been obtained for all the stable isotopes of 12 elements, and also for several radioactive isotopes.

The situation is less favorable for elements contained in polyatomic molecules. Here the same problems are encountered which have prevented the determination of molecular parameters with the accuracy that the high precision of microwave measurements would seem to imply. Even for the simplest molecules it is experimentally difficult to obtain the complete set of anharmonic constants necessary for extrapolation to the vibrationless state, and theory is not yet in a position to be very helpful. Though mass ratios cannot, in general, be obtained precisely from data on polyatomic molecules, ratios of mass differences appear to be calculable with good accuracy in many cases. For a detailed discussion of microwave mass determination and for numerous references to experimental work the reader is referred to the excellent recent review by Geschwind, Gunther-Mohr & Townes (175).

Techniques and Instrumentation

Though no revolutionary development in instrumentation has occurred in the past year, significant progress has been made and some probable trends appear to be indicated. The more ready availability of diffraction gratings, and particularly those which concentrate intensity in the blaze, has made possible the observation of the Raman spectra of gases under very high resolution (78, 79), and a more widespread use of gratings in infrared spectros-

copy. As has been demonstrated by Gaunt (198) and Cole (199), it is possible with a single grating to cover the complete spectral range usually investigated in infrared work. For the same coverage, several expensive prisms are required to obtain comparable resolution throughout. It seems very possible that in the near future gratings will be employed for general survey work. To do this conveniently and automatically will require some ingenuity, if undue complexity is to be avoided, since the coupling of a foreprism to eliminate overlapping grating orders presents problems. The alternative use of filters is attractive and is perfectly feasible in the near infrared. However, filters presently available for the region of longer waves commonly have the characteristic that the region of transition from practical opacity to reasonable transmission covers more than one octave, which renders them unsatisfactory for use with gratings. For example, the *F*-center filters which have recently been developed (198, 200) have this property. The use of Christiansen filters for the isolation of moderately long waves has been described by Hadni (201).

The use of the double or multipass principle in infrared spectrometers to improve resolving power and reduce stray light is becoming quite common, and several methods have been suggested whereby the double pass and the double beam or other ratio recording arrangement can be combined (202, 203, 204). Quite recently the region extending from the edge of the visible to about 3 μ has been made available under moderate or high dispersion in several commercial spectrometers and renewed interest in this region may be expected.

Though infrared spectroscopy and particularly applied spectroscopy owe an enormous debt to the recent improvements in instrumentation embodied in commercially available spectrometers, it is perhaps worth pointing out that there is always some possibility that the course of research may be dictated by certain limitations imposed by these instruments.

In the field of microwaves several developments are in progress which are extending the capacity of this branch of spectroscopy. High temperature spectrometers have been described by Stitch *et al.* (205) and by Tate & Strandberg (206) which make high boiling substances available for study. The extension of measurements to higher frequencies has been described by King & Gordy (162). Great improvement in resolving power has been effected through a combination of molecular beam and microwave techniques. Strandberg *et al.* (207, 208), by observing the ammonia inversion absorption in a direction transverse to an unfocused ammonia beam, succeeded in reducing the normal Doppler width by a factor of 6. Gordon, Zeiger & Townes (209) have described a device in which a focused ammonia beam is captured in a tuned cavity. When this was used as a microwave spectrometer, line widths of 6 to 8 kc. were obtainable. Techniques of this kind are free from some limitations of the ordinary molecular beam method (i.e., the necessity for detecting molecules) and offer promise in the study of refractory materials and free radicals.

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METAL CHELATE COMPOUNDS[1,2]

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EQUILIBRIUM CONSTANTS

The main activities in the field of metal chelate compounds in recent years have centered around the accumulation of a large number of stability constants. At the present time sufficient equilibrium data are available to allow a preliminary survey of the general significance of the results, and its bearing on present concepts of the nature of metal chelate compounds. Although this review will be concerned primarily with recent interpretations of stability constants, consideration will also be given to new advances in experimental methods, reaction mechanisms, catalysis, metal titrations, and various developments of probable future significance.

Experimental Methods

The majority of the metal chelate formation constants K_f now being reported are so-called "concentration constants," measured in a controlled ionic medium, usually at an ionic strength of 0.010. Although polarographic and spectrophotometric methods are useful in many cases, potentiometric methods seem to be the most versatile and are the most widely used.

The mercury electrode.—The electrodes which have been found generally applicable to equilibrium measurements of coordination compounds are only three in number: the hydrogen electrode (or its counterpart, the more widely-used glass electrode), and the silver-silver chloride and calomel electrodes. Recently, Schwarzenbach (1) has extended the use of the Hg, Hg^{++} electrode to the measurement of metal chelate formation constants, many of which are too high to be determined by direct measurements of hydrogen ion concentration. The principle of the method lies in the participation by another metal ion in the equilibrium: $Hg^{+2}+A^{-m}\rightleftharpoons HgA^{2-m}$. From the emf. of the Hg, Hg^{++} electrode with and without the second metal, and the formation constant of HgA, the formation constant of MA may be calculated. The value of E° for the cell Hg, Hg_2^{+2} was reported as -0.796 v. at 25°C., and for the reaction $Hg_1+Hg^{+2}\rightleftharpoons Hg_2^{+2}$, at 25°, K was found to be 83 ± 2, in agreement with the corrected value given by Latimer (2).

Mixed solvents.—The extension by Calvin & Wilson (3) of stability constant measurements to the mixed solvent 50 per cent dioxane–50 per cent water (by volume) has been substantiated and further extended by Van Uitert & Haas (4) to the whole range of concentration of this solvent system up to 75 volume per cent dioxane. At the latter concentration, as well as at

[1] The survey of the literature pertaining to this review was concluded in December, 1954.

[2] The following abbreviations will be used: EDTA, ethylenediaminetetraacetic acid; NTA, nitrilotriacetic acid; tren, triaminotriethylamine.

intermediate solvent compositions, pH meter readings were found to be linear with hydrogen ion concentration, except at the extremes of strongly alkaline and strongly acidic solutions, and the slope of $-\log H$ versus pH meter reading was found to be normal. It was suggested that the pH meter reading, B, be corrected to infinite dilution by the term $\log U^{\circ}_{H}$, according to the relationship: $-\log (H^{+}) = B + \log U^{\circ}_{H}$, the value of $\log U_{H}$ being set at zero in pure water. In Figure 1 is given the variation of U°_{H} with solvent composition for pH meter measurements of glass versus calomel electrodes, and the corrections obtained when the calomel electrode is replaced by a Ag–AgCl electrode. The difference between the two curves indicates the variation in the liquid junction potential with solvent composition, while $U^{\circ\prime}_{H}$ indicates the influence of solvent on activities of hydrogen and chloride ions and on the asymmetry potential of the glass electrode.

Thermodynamic constants.—Since concentration constants may vary by a factor of 10 or more with changes in ionic concentration, it is not surprising that stability constants published by various investigators without correction to zero ionic strength are frequently in disagreement. Recently Izatt *et al.*, (5) have made a beginning toward conversion of existing data to thermodynamic constants by calculating activity coefficients with equations of the type:

$$-\log f_i = \frac{AZ_i^2\mu^{1/2}}{1 + Ba^*\mu^{1/2}} \qquad 1.$$

where A and B are calculated as described by Manov *et al.* (6) and by Harned & Owen (7), and the other terms have their usual meaning. Considerable uncertainty exists in the assumption of a value for a^*, the distance of closest approach, since it does not have any clear relationship to ionic dimensions. Izatt *et al.* assumed a value of 10 Å for all substances treated. Good agreement between the corrected constants calculated from concentration constants corresponding to different ionic strengths was taken as an indication of the reliability of the result. Although thermodynamic constants obtained in this way are a considerable improvement over the uncorrected values, there are many uncertainties in the method, such as change of activity coefficient with a change in the ratio of ionic species present, unknown changes in liquid junction potentials, and failure of the above equation for dipolar ions and for anions containing a number of polar groups.

A different approach to the determination of thermodynamic formation constants, recently reported by Carini & Martell (8) and by Hughes & Martell (9), is the Debye-Hückel-guided extrapolation of potentials of cells of the type

$$\mathrm{Pt—H_2,\quad K^+}(m_1),\quad \mathrm{M^{+}_{2}}(m_2),\quad \mathrm{Cl^-}(m_3),\quad H_nV^{n-m}(m_4),\quad \mathrm{AgCl—Ag}$$

where H_mV is the acid form of a ligand such as ethylenediaminetetraacetic acid or nitrilotriacetic acid. The relationship for the thermodynamic constant is:

$$\mathrm{pwH} - \tfrac{1}{2}(\mathrm{pK_3} + \mathrm{pK_4}) + \tfrac{1}{2}\log\frac{m_M \cdot m_{H_3V}}{m_{MV}} = -\tfrac{1}{2}\log K_{MV} - \tfrac{1}{2}\log\frac{\gamma_M\gamma_{H_3V}\gamma_{Cl^-}}{\gamma_{MV}} \qquad 2.$$

The quantities on the left side of equation 2 were determined experimentally, and the activity quotient on the right was calculated in the usual manner as described by Hamer & Acree (10). Since this term becomes zero on extrapolation to infinite dilution the parameter a^* (see equation 1) was arbitrarily chosen so as to give a linear extrapolation of smallest possible slope. The resulting thermodynamic constants do not depend on the calculation of activity coefficients, which are eliminated in the extrapolation. On the other hand, this method cannot be used for the calculation of concentration constants, since the true activity coefficients of the species involved are not known.

Formation constants from displacement reactions.—The potentiometric method, which is used to measure formation constants through the displacement of hydrogen ions from the ligand by the metal ion, cannot be used when the stability is so great that the chelate is not appreciably dissociated in acid solutions. In such instances it is possible to determine stability constants by displacements of either (*a*) one ligand by another, or (*b*) one metal ion by another.

Method (*a*) has been developed by Schwarzenbach (11) for the determination of transition metal chelates of ethylenediaminetetraacetic acid (EDTA) and of nitrilotriacetic acid (NTA), and the same procedure was employed by Chaberek & Martell (12) for the determination of stability constants of transition metal chelates of hydroxyethylethylenediaminetriacetic acid. The second ligand, triaminotriethylamine, (tren) was chosen because of its greater basicity and greater dissociation of its chelate in acid solution. Thus, by measurement of the equilibrium constant K_E of the following reaction:

$$H_3tren^{+3} + MY^{n-m} + M'^{+2} \rightleftharpoons M'Y^{2-m} + Mtren^{+m} + 3H^+,$$

it is possible to determine the stability constant of MY^{n-m} from the relationship $K_{MY} = K_{M'Y}K_{Mtren}K_1K_2K_3/K_E$ if the successive acid dissociation constants K_n of tren, and the chelate formation constants $K_{M'Y}$ and K_{Mtren} are known. This procedure may be used for the determination of metal chelates with a wide range of stabilities by proper selection of the second metal ion M′ and the use of secondary ligands other than tren.

Method (*b*), involving the competitive reactions of two metal ions for a ligand, is the basis of the use of the mercury electrode, described above, by Schwarzenbach & Anderegg (1). The displacement of one metal by another has also been followed spectrophotometrically by Hughes & Martell (13) and polarographically by Bril & Krumholz (14). The spectrophotometric method suffers from the disadvantage that it is limited to systems in which at least one reacting component is highly colored and for which the relative stability constants differ by less than 10^2. However, good agreement was obtained by the latter two methods for the stabilities of the transition metal–EDTA chelates. The polarographic method has been used by Schwarzenbach *et al.* (15) in the determination of stabilities of a large number of metal

chelates of ethylenediaminetetraacetic acid and 1,2-diaminocyclohexanetetraacetic acid.

Empirical Correlations

Influence of metal ion.—Van Uitert *et al.* (16, 17) have made extensive correlations of chelate stability constants with metal ion electronegativities reported by Haïssinsky (18). The stability constants of various divalent metal chelates of β-diketones, determined in 75 volume per cent dioxane–25 per cent water mixtures by Van Uitert, Fernelius & Douglas (16) were found to vary in a linear manner with electronegativity of the metal ion, as is indicated in Figure 2, and the slopes of the lines increased with the charge of the metal ion. Additional reduction of the data was obtained by assuming that the slopes of these lines should be proportional to the relative strengths of the bond hybrids: 1.0, 2.0, 2.7, and 3.0 for s, sp^3, dsp^2, and d^2sp^3 bonds, respectively. Thus, a plot of log K_f as a function of the electronegativity–bond orbital strength product was found to approximate a straight line, as is indicated in Figure 3. Regardless of its theoretical significance, this graph is important as the first reduction to a single linear function correlating chelating tendencies of such a wide variety of metal ions.

Other correlations, relating stabilities of metal chelates with ionization potentials of the metal, have been given by Irving & Williams (19, 20), Calvin & Melchoir (21), Schwarzenbach *et al.* (22, 23) and Martell & Calvin (24). Recently Calvin (25) has demonstrated the equivalence of ionization potential and electronegativity–hybrid bond strength product as measures of chelating tendencies. His correlation of the stabilities of dibenzoylmethane chelates of metal ions of various charge type, given in Figure 4 is remarkably similar to that of Van Uitert & Fernelius (17) given in Figure 3.

Structure of the ligand.—A semiquantitative estimate of the stabilizing influence of metal chelate rings on coordination compounds was first made by Calvin & Wilson (3) and later by Martell & Calvin (26). Concurrently, Schwarzenbach (27, 28) reviewed the evidence for a large number of compounds, and has elaborated the concept of enhanced stability resulting from the formation of chelate rings. His theory, called the "chelate effect" is illustrated by the examples listed in Table I, which indicates that the stability of a coordination compound is appreciably greater than the stability of an analogous substance which differs from it primarily in that it contains one less ring. By the use of a simplified model in which the binding energies of a metal ion to two monodentate ligands, A, was assumed to be the same as the energy of binding to a bidentate ligand, A—A, he was able to show that the formation constant of the chelate M—A—A would be greater than that of the complex MA_2 and that the difference between the two would be expected to decrease with increasing length of the chain. It was also demonstrated that the predicted stability differences are of the same order of magnitude as the values found experimentally.

Van Uitert & Fernelius (29) have correlated chelate stabilities with ligand properties by plotting log $K_{Ni} - \log K_{Mg}$ against log K_{Ni}. Points corresponding to ligands with similar donor groups were found near lines of characteristic slope, as is indicated in Figure 5. This is an interesting variation of a similar correlation against acid dissociation constant of the ligand, which previously was used extensively by other investigators such as Calvin & Wilson (3), Schwarzenbach *et al.* (22), Martell & Calvin (30) as well as Bryant, Fernelius & Douglas (31).

The two correlations given above of formation constants with properties of the ligand may be said to complement each other. Schwarzenbach's chelate effect provides a basis for increase in stability with an increase in the number of metal chelate rings; and the correlation by Van Uitert & Fernelius

TABLE I

STABILITY INCREMENTS RESULTING FROM SUBSTITUTION OF TWO MOLES OF IMINODIACETATE BY ONE MOLE OF ETHYLENEDIAMINETETRAACETATE

Metal Ion	log K_{MA_2}*	log K_{MB}†	log $K_{MB} - \log K_{MA_2}$
Ca(II)	5.4	10.6	5.2
Cd(II)	10.0	16.5	6.5
Fe(II)	10.1	14.0	3.9
Zn(II)	12.2	16.0	3.8
Co(II)	12.3	16.2	3.9
Ni(II)	14.6	18.2	3.6
Cu(II)	16.1	18.5	2.4

* A = iminodiacetate.

† B = ethylenediaminetetraacetate.

of log $K_M - \log K_{M'}$ versus log K_M, where the electronegativity of metal ion ion M is much greater than that of M′, applies to ligands which do not differ greatly in the nature and positions of the donor groups. Thus, the chelate effect seems to give the best correlation of the stability difference between I and II, while the linear plots of Van Uitert & Fernelius apply to series of related compounds such as III and IV (see Plate I), the stabilities of which are modified by changing the substituents R and R'.

SIGNIFICANCE OF STABILITY CORRELATIONS

The abundance of stability data and a wide variety of possible empirical correlations have resulted in a number of conflicting and contradictory views concerning the nature of metal chelate compounds.

Electronegativity of metal ion.—The correlation by Van Uitert *et al.* (16, 17) between free energy of metal chelate formation and the product of electronegativity and hybrid orbital bond strength assumes that only covalent bond energies are important and neglects the entropy change. The

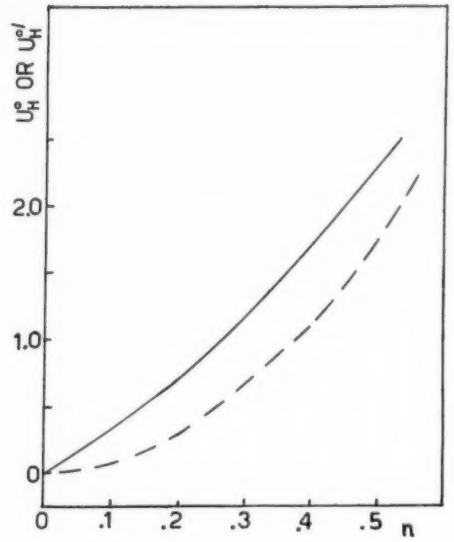

FIG. 1. Variation of pH meter corrections with solvent composition: n, mole fraction of dioxane; solid line, glass versus calomel electrode; dashed curve, glass versus Ag–AgCl electrode.

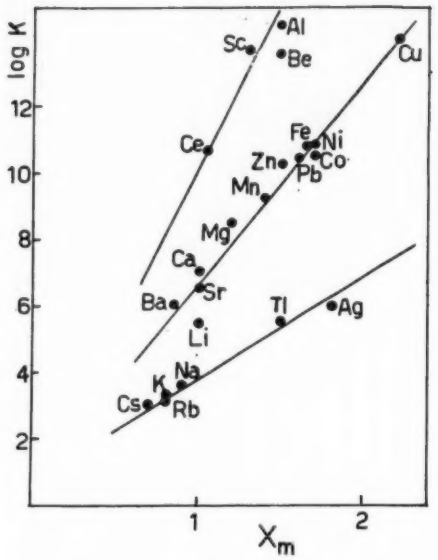

FIG. 2. Correlation of stabilities of dibenzoylmethane chelates with metal ion electronegativities.

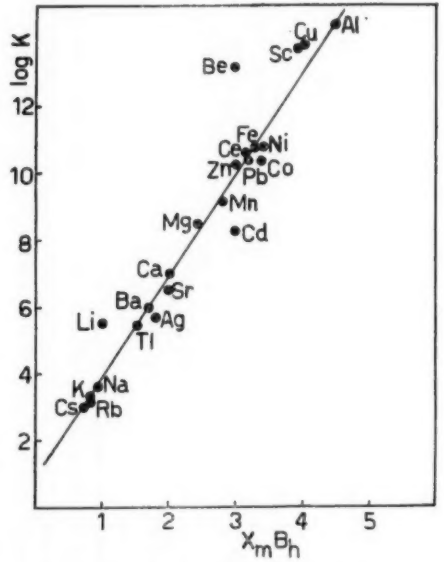

FIG. 3. Correlation of stabilities of dibenzoylmethane chelates with product of electronegativity and hybrid bond orbital strength.

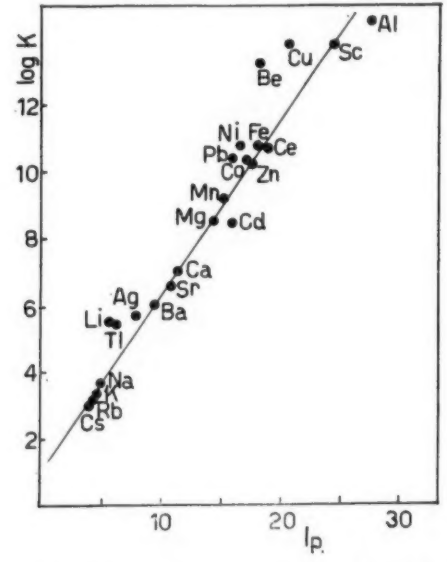

FIG. 4. Correlation of statilities of dibenzoylmethane chelates with ionization potentials of metals.

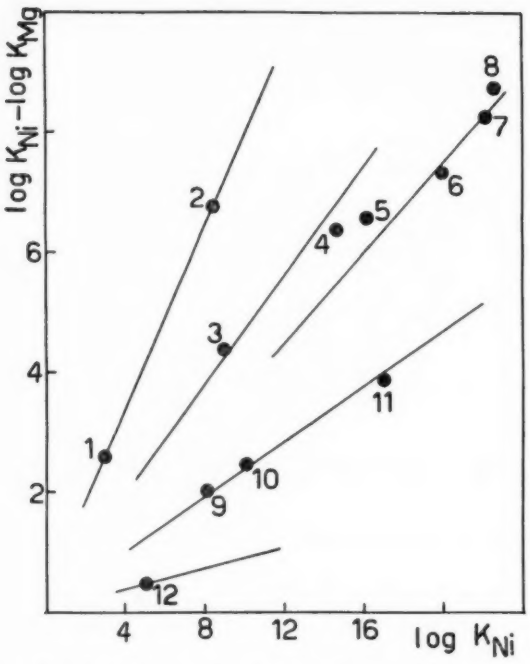

FIG. 5. Log $K_{Ni} - \log K_{Mg}$ versus log K_{Ni} for various ligands: 1, ammonia; 2, ethylenediamine; 3, glycine; 4, 8-hydroxyquinoline; 5, 1-(2-hydroxy-5-methylbenzeneazo)-2-benzoic acid; 6, 1-phenyl-3-methyl-4-(2-hydroxy-4-sulfonic acid-naphthylazo)-5-pyrazolone; 7, 1-(2-hydroxy-5-chlorobenzeneazo)-α-naphthol; 8, 1-(2-hydroxybenzeneazo)-2-naphthol; 9, salicylaldehyde; 10, acetylacetone; 11, D-tartaric acid (3 protons removed); 12, salicylic acid.

latter, however, must become relatively more important with the small free energy changes usually involved in the formation of coordination compounds, particularly when the combination of positive and negative ions is involved. Powell & Latimer (32) have shown that the entropies of aqueous metal ions may be expressed by the equation

$$\bar{S}^0 = (3/2)\, R \ln M + 37 - 270Z/r_e^2 \qquad 3.$$

where Z is the charge and r_e is the crystal radius + 2.0 Å. It is not unreasonable to conclude that the increase in entropy resulting from the displacement of two bound water molecules from metal ions of about the same radius, would be approximately proportional to the charge of the ion. Thus, it is rather likely that entropy contributions to stability would not result in

appreciable scatter from the lines in Figure 2, which have slopes that are proportional to the charge of the metal ions. The abnormally high stabilities for Li^{+} and Be^{++} could result from the lower entropy of these metal ions as a consequence of their low atomic weight (M of equation 3) and unusually small radii.

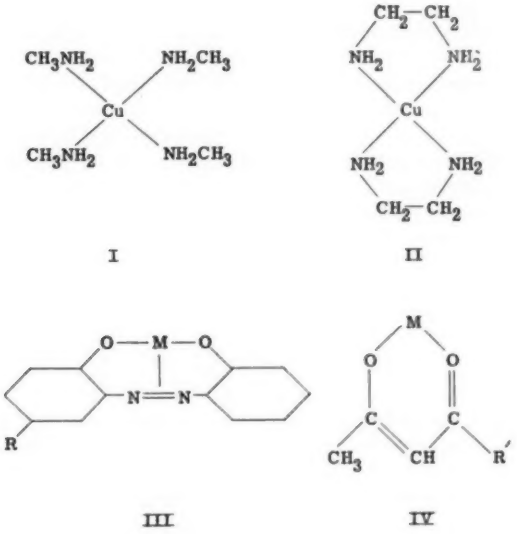

PLATE I.

The use of relative hybrid bond orbital strengths as a parameter in Figure 3 was based on the assumption that the free energy changes would depend on overlap of atomic orbitals of the metal with those of the ligand. Therefore, metal ions were assumed to form coordinate bonds with the following types of orbitals; monovalent ions, s; divalent ions, sp^3 (excepting Pd, dsp^2); and trivalent ions, d^2sp^3. As has been pointed out by Coryell (33), it is unlikely that such a wide variety of metals would show such uniform behavior with respect to bonding orbitals. However, it is unlikely that s orbitals of the alkali metal ions do not involve some p hybridization, that d orbitals are not involved in the transition metal chelates, and that "outer" sp^3d^2 orbitals are not important for many of the transition and heavy metal ions. Coryell (33) has further offered the interesting suggestion that since the hybrid bond orbital strengths, X_m, are essentially equivalent to the charge of the ion, binding energy may be controlled by ion-dipole forces which are propor-

tional to the charge. Thus, X_M in the abscissa of Figure 3 might well have been ionic charge. However, Figure 4 indicates that the ionization potential sum produces as satisfactory a reduction of the data. Correlation with electronegativity amounts to comparison with the heat of reaction $M^{+n}(s) + (n/2)Cl_2(g) \rightarrow MCl_n(s)$, upon which the electronegativity values are based. So, the ionization potential may be considered at least as meaningful as electronegativity. However, neither concept can be considered theoretically significant without more detailed information on the enthalpy and entropy changes involved in the formation of these metal chelates.

Electronegativity of ligand.—In accordance with the suggestions of Walsh (34), Van Uitert & Fernelius (29) state that log K_f should increase with the electronegativities X_m' and X_c, of the metal ion and ligand, and decrease with increasing electronegativity difference $X_m' - X_c$. They also considered the bond-weakening influence of nuclear repulsion on wave function overlap when the electronegativities of the partners becomes too great. By neglecting entropy effects, and using arguments not entirely clear to the reviewer, Van Uitert & Fernelius conclude that the slopes of the lines in Figure 5 indicate the following order of electronegativities of the coordinating ligands involved:

$$-COO^-, -O^- > -O^-, =O > -N=N, 2-O^- > \diagup\!\!\!=\!\!\!\diagdown N, -O^- > -\overset{|}{N}-$$

This is the order of increasing affinity for metal ions. It would be of interest to have this approach to relative activities of ligands placed on a sounder basis, the above series being complicated by the fact that ligands with varying geometry and numbers of donor groups were employed.

Entropy effects.—Since the model used by Schwarzenbach (27) involved a comparison between a metal chelate and a similar nonchelated compound with the same binding energy between the donor groups and the metal ion, the greater stability of the metal chelate necessarily seemed to be an entropy effect. However, Williams (35) has disagreed with this interpretation of the stability of metal chelate compounds, and places greater stress on the favorable heat of chelate formation resulting from the reduction of repulsive force between the neighboring donor groups in a chelate compared with similar forces between neighboring monodentate ligands in a complex. There is no doubt that the enthalpy term is important in many cases, since the repulsive forces between two donors already bound together by a short linkage will not have to be overcome in the formation of the metal chelate.

If the entropies of all reacting species follow the empirical relationships given by Powell & Latimer (32), Connick & Powell (36), and by Cobble (37, 38), the reactions $M^{+2} + 2A^- \rightarrow MA_2$ and $M^{+2} + A-A^{-2} \rightarrow \overset{\lceil\rceil}{M-A-A}$ would involve nearly the same entropy change and there would be no chelate effect beyond a small statistical factor. On the other hand, Powell & Latimer (32) have indicated that the entropies of organic substances containing hy-

drogen-bonded polar groups may be abnormally low, and Cobble (38) has suggested that the entropies of metal chelate compounds may be unusually high, since the polar groups of the ligand are directed toward the metal ion so that the chelate presents a "hydrocarbon shell" to the solvent. A combination of these two factors might result in an appreciable chelate effect. Thus, the fact that the entropy of the oxalate ion is considerably less than one would calculate from two formate ions indicates the possibility of a stabilizing entropy (chelate) effect, provided that the entropies of the products are comparable.

Unfortunately, it is not yet possible to test these theories experimentally since only a small amount of thermodynamic data on metal chelate formation have thus far been published. Also, many of these data are inaccurate since they have been obtained from equilibrium constants without correction to zero ionic strength. Some of the thermodynamic quantities now available are given in Table II. Other partial listings have been given by Williams (35) and by Cobble (38). Important contributions have recently been made to the behavior of the diamines by Spike & Parry (39) and by Basolo & Murman (40). The heats and entropies given by Basolo & Murman for the Cu(II) and Ni(II) chelates of ethylenediamine and of its monomethyl and diethyl derivatives seems to have a bearing on the suggestions of Williams (35) and of Cobble (38) mentioned above. As the alkylation of the nitrogen atoms increases, the enthalpy contribution to chelate stability decreases as the result of steric repulsions between ligands, whereas the entropy contribution to stability increases as the result of more effective screening of the central ion from the solvent.

For the more basic metal ions, such as the alkaline earth metal ions, the data of Table II indicate that the bond energy between the metal and ligand is little different from the energy of binding of the displaced water molecules, and that the stabilities of the corresponding metal chelates are due almost entirely to entropy changes. It is also apparent from the empirical relationships given by Powell & Latimer (32), Connick & Powell (36), and by Cobble (37), that a favorable entropy change occurs when chelate formation is accompanied by a decrease in charge. This was also emphasized by Williams (35), and is apparent from many of the examples in Table II.

Perhaps the most urgent need in the field of metal chelate compounds is a large variety of accurate thermodynamic formation constants and enthalpies of reaction obtained from calorimetric measurements as well as temperature coefficient data. Until such information is available, it will not be possible to understand the relative effects of covalent binding and entropy factors on the stability of chelate rings.

OTHER DEVELOPMENTS

Reaction Mechanisms

Substitution reactions.—Considerable interest has developed in recent years concerning the mechanism of substitution reactions in covalently-

TABLE II

THERMODYNAMIC CHANGES ASSOCIATED WITH THE FORMATION OF METAL CHELATES IN AQUEOUS SOLUTION

Metal Ion	Ligand	Formula of Product[a]	$\Delta F°$[h] kcal./mole[h]	$\Delta H°$ kcal./mole	$\Delta S°$ cal./°C.	Ref.
Fe(III)	$C_2O_4^{-2}$	MA^+	−13.2[i]	− 0.3	+43	41
Mg(II)	malonate^{-2}	MA	− 4.0[l]	+ 3.2	+24	42
Zn(II)	malonate^{-2}	MA	− 5.0[l]	+ 3.1	+27	42
Ni(II)	en[b]	MA_2^{+2}	−18.1[j]	−16.3	+ 7	40
Cu(II)	en	MA_2^{+2}	−26.6[j]	−24.6	+ 7	40
Ni(II)	N-Me-en[c]	MA_2^{+2}	−17.2[j]	−17.0	+ 1	40
Cu(II)	N-Me-en	MA_2^{+2}	−25.3[j]	−23.0	+ 8	40
Ni(II)	$(N\text{-Et})_2$en[d]	MA_2^{+2}	−15.3[j]	− 7.8	+27	40
Cu(II)	$(N\text{-Et})_2$en	MA_2^{+2}	−23.3[j]	−17.5	+21	40
Ni(II)	trien[e]	MA^{+2}	−14.9[k]	−13	+23	43
Cu(II)	trien	MA^{+2}	−28.7[k]	−22	+22	43
Mg(II)	NTA[f]	MA^-	− 8.94[l]	+ 4	+44	9
Ca(II)	NTA	MA^-	−10.36[l]	0	+31	9
Ba(II)	NTA	MA^-	− 8.00[l]	+ 1	+23	9
Mn(II)	NTA	MA^-	−11.73[l]	+ 2	+46	9
Mg(II)	EDTA[g]	MA^{-2}	−12.4[l]	− 3	+32	8
Ca(II)	EDTA	MA^{-2}	−15.0[l]	− 3	+42	8
Sr(II)	EDTA	MA^{-2}	−11.9[l]	− 4	+26	8
Ba(II)	EDTA	MA^{-2}	−10.5[l]	− 4	+22	8
Mn(II)	EDTA	MA^{-2}	−17.2	− 5.2	+41	44
Co(II)	EDTA	MA^{-2}	−21.4	− 4.1	+58	44
Ni(II)	EDTA	MA^{-2}	−24.0	− 7.6	+55	44
Cu(II)	EDTA	MA^{-2}	−24.4	− 8.2	+55	44
Zn(II)	EDTA	MA^{-2}	−20.9	− 4.5	+55	44
Cd(II)	EDTA	MA^{-2}	−20.5	− 9.1	+38	44
Pb(II)	EDTA	MA^{-2}	−23.6	−13.1	+35	44

[a] Formulas indicate ratio of ligand to metal ion and charge of chelate.
[b] Ethylenediamine.
[c] *N*-methylethylenediamine.
[d] N,N′-diethylethylenediamine.
[e] Triethylenetetramine.
[f] Nitrilotriacetate.
[g] Ethylenediaminetetraacetate.
[h] Temperature = 25° C. unless otherwise specified.
[i] Communicated by H. Williams (35), no temperature given.
[j] 0°.
[k] 35°.
[l] Extrapolated to infinite dilution.

bonded complex ions.[3] The subject was brought up to date three years ago in a review by Taube (45). The bimolecular substitution reactions of such square-planar complexes as $Ni(CN)_4^{-2}$, $Pd(CN)_4^{-2}$, and PtX_4^{-2} have been interpreted by Adamson (46) and Taube (45) as a bimolecular reaction to form a five-coordinated transition state employing the available outer *p*-orbital. A similar interpretation involving a seven-coordinated intermediate was also suggested by Adamson (46, 47) and by Taube (45) for substitution reactions of hexacoordinated octahedral complexes. In addition to the bimolecular S_N2 mechanism, there is also the possibility of a monomolecular S_N1 mechanism involving a first-order dissociation to give a five-coordinated intermediate. Recently Brown *et al.* (48, 49, 50) have suggested, as an alternative mechanism for S_N2 substitution reactions, an edge-displacement in which the entering group causes the shift of another ligand to the position from which a third group is displaced. This interpretation and the alternative S_N1 dissociation are outlined in Plate II as two probable routes for substitution reactions of octahedral complexes.

On the basis of second-order kinetics of the hydrolysis of $Co(NH_3)_5Br^{+2}$ reported by Bronsted & Livingston (51) and by Olson & Simonson (52), and their own findings of second-order kinetics in the substitution of Cl^- in *cis* $Co(en)_2Cl_2^+$ by various anions, Brown & Ingold (49) suggested S_N2 mechanisms for these reactions. They further indicate a transition from an S_N1 mechanism (slow) to a more rapid S_N2 type of reaction as the basicity of the attacking ion increases. Thus, the transition from an S_N1 mechanism for bromide and thiocyanate to an S_N2 mechanism for azide, nitrite, and methoxide, illustrated in Figure 6, is analogous to a similar mechanistic change known to occur in substitution reactions on a saturated carbon atom. On the other hand, Adamson & Wilkins (53) have pointed out that catalysis of the formation of the S_N1 intermediate by ion-pair formation might also give second-order displacement kinetics in these compounds.

Brown *et al.* (48) have described the stereochemical course to be expected on the basis of their proposed edge-displacement theory, and showed that it accounts for the observed sterochemical phenomena. They have also pointed out the unreliability of present assignments of configuration of octahedral complexes and the need for a thorough reinvestigation of the sterochemistry of octahedral coordination compounds.

Catalytic properties.—Since the review of catalytic properties of metal chelate compounds by Martell & Calvin (54) and by Calvin (25), there has been less activity in this field than seemed to have been warranted by the

[3] Although many of the substances investigated cannot be classified as chelate substances, it is believed that developments in this research field are fundamental to the understanding of the nature of chelate compounds, and are particularly important in their applications to the behavior of catalytically active metal chelates such as those described in the next section.

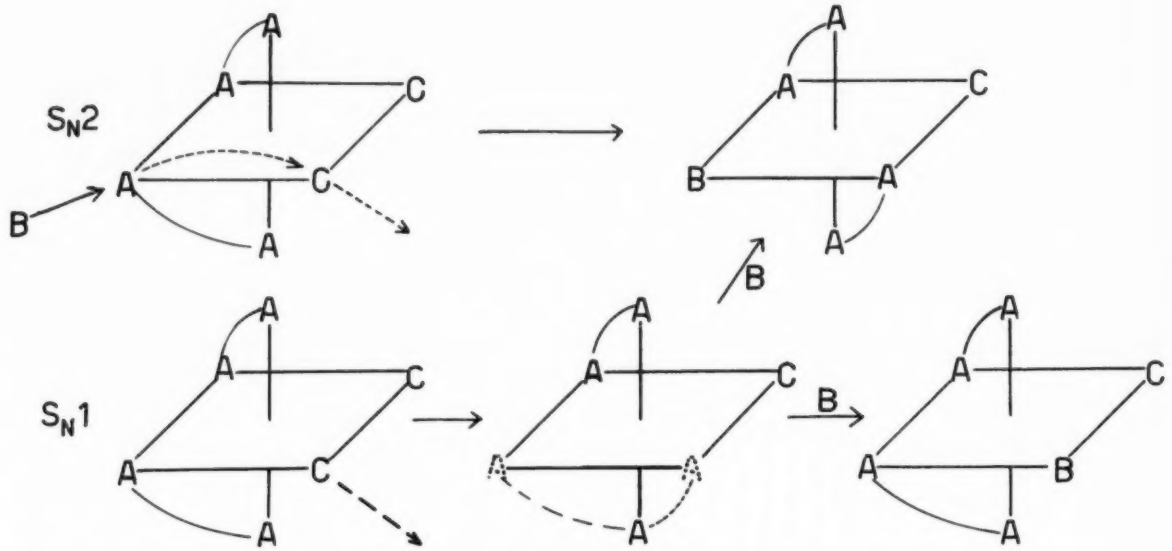

PLATE II. Probable routes for substitution reactions of octahedral complexes.

large number of possibilities and important applications to biochemical reactions. The most significant advance has been an elucidation of the catalytic effects of vitamin B_6-catalyzed reactions and metal chelate models of these enzyme systems.

Metzler, Ikawa, & Snell (55) have pointed out the characteristics of the metal-pyridoxal chelates required to show pyridoxal phosphatase enzyme activity. Formula V (see Plate III) illustrates the combination of an active metal chelate combined with an α-amino acid through Schiff base formation:

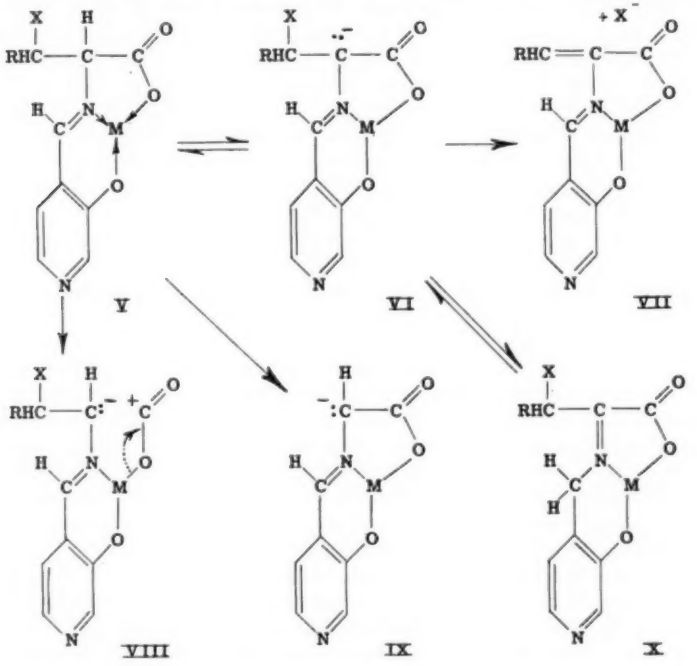

PLATE III. Examples of conversions occurring in metal chelate models of vitamin B_6-catalyzed reactions (ring substituents omitted from pyridoxal for clarity).

In the presence of Cu^{+2}, Fe^{+3}, or Al^{+3} as the activating metal ion, M, the reactions may proceed in four different ways, as follows: (*a*) the electron attracting influence of the metal ion may result in an electron shift in compound V toward the nitrogen with decarboxylation. The product (VIII) on hydrolysis yields pyridoxamine and an aldehyde. (*b*) the electron attraction of the metal ion may also result in the formation of a reactive intermediate (VI) by the elimination of a proton from the α-carbon atom, and is converted to X by simultaneous addition of a proton to the carbonyl carbon.

Hydrolysis of compound X results in the formation of the pyridoxamine chelate and an α-keto acid, and the reversible equilibrium between V and X represents a typical transamination reaction. (*c*) The reactive intermediate VI may also be stabilized by elimination of group X from the β-position to form VII, which then hydrolyzes to an α-keto acid and ammonia. (*d*) The elimination of group RCHX from V can take place to give an aldehyde and IX, which can hydrolyze to glycine and pyridoxal or glyoxylic acid and pyridoxamine.

The various reactions of pyridoxal-containing enzymes reviewed by Snell (56) include reactions of type *a* to *d*. An example of model reaction *b* is found in the nonenzymatic decarboxylation of histidine to histamine described by Werle & Koch (57). Nonenzymatic transmination reactions, type *b*, have been reported by Metzler *et al.* (58, 59). Reversible reactions of type *c* have been reported by Metzler *et al.* (60, 61) in the splitting of threonine to glycine and acetaldehyde and of serine to glycine and formaldehyde. Examples of type *d*, consisting of the elimination of OH from serine and SH and SR from cystein and cystathionine, have also been reported by Metzler *et al.* (55, 61). Ikawa & Snell (62) have demonstrated by inference the importance of the inductive effect of the aromatic nitrogen atom in pyridoxal by showing that 4-nitrosalicylaldehyde produced models having activity similar to that of pyridoxal, but that less electronegative benzene derivatives showed no catalytic activity.

Absorption spectra.—A considerable advance in the understanding of visible and near infrared absorption spectra of coordination compounds, has been made by Bjerrum *et al.* (63) and Jorgensen (64) using the treatment of Orgel (65) which was based on the crystal-field theory of Bethe (66). A qualitative picture developed in Figure 7 shows the electronic energy levels E as a function of the external field π of the ligand dipoles. For the gaseous ion ($\pi = 0$) a transition metal is indicated as having, for example, three degenerate levels, ^4X, ^4Y, and ^2Z with spin quantum numbers 3/2, 3/2, and 1/2, respectively. The splitting is approximately proportional to π, the number of levels increasing with L of the original term and with decreasing symmetry of the field. Transitions between the ground state and higher levels of the same multiplicity are the most probable, and give rise to bands of ordinary intensity. The "forbidden," or less probable, transitions where S changes by 1 have intensities of about 1 per cent of ordinary absorption bands. This concept was used by Jorgensen (64) in explaining the number and positions of low-intensity absorption bands of transition metal complexes (and chelates) on the basis of the known atomic levels and various models for arrangement of ligand dipoles. It was found that octahedral models gave satisfactory agreement with experimental results for the first-row transition metals except in the case of Ni(II) and Cu(II) ions, for which tetragonal models were required.

Bjerrum *et al.* (63) were successful in using their extension of the crystal-field theory to explain the positions of the two observed absorption bands of

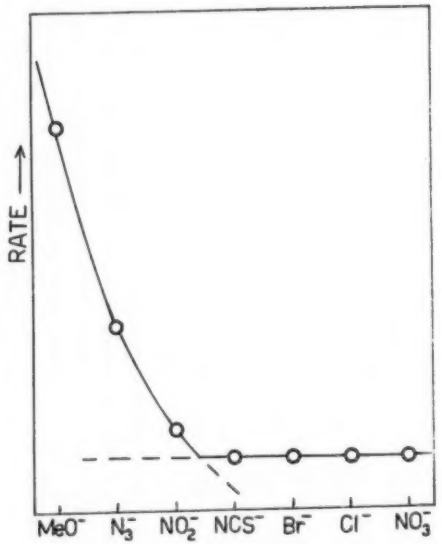

FIG. 6. Kinetic relations applying to substitution of *cis*-$(Co(en)_2Cl_2)^+$ by negative ions.

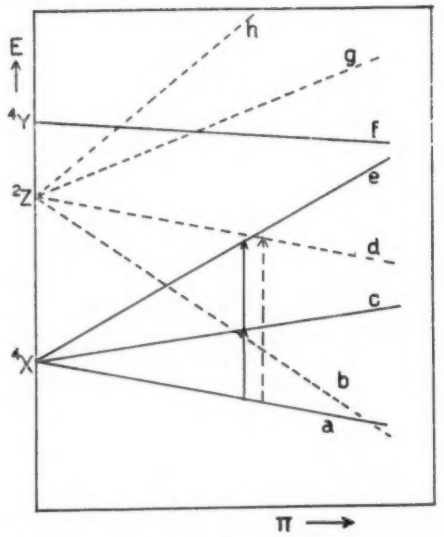

FIG. 7. Energy E as a function of perturbation strength Π, terms ^4X, ^4Y, and ^2Z of the free ion arbitrarily chosen. Vertical lines represent probable —, and improbable - - - - - transitions (Orgel diagram).

Cu(II)-ammine complexes. By assuming reasonable values of interatomic distances and dipole moments of the ligands, they were able to show that only an octahedral model, in which two of the distances are a few per cent greater than the rest, gave predictions in agreement with experiment.

Polynucleate complexes.—Sillén (67) has recently proposed general relationships for equilibria involved in the formation of polynucleate complexes, and has described how experimental data may be treated to determine the formulas of the substances formed. Hietanen & Sillén (68) have applied these general relationships to the special case of hydrolysis of a metal ion, and have deduced general formulas for a series of polynuclear hydroxy complexes. The general structures of these substances seem to conform to a general "core plus links" formula, in which a series of similar groups, containing hydroxide and metal ion, are attached to a single ion which forms the beginning (or center) of the polynucleate chain or network. Some of the formulas so deduced are $Bi^{+3}((OH)_2Bi)_n^{3+n}$, $Fe((OH)_2Fe)_n^{3+n}$, $UO_2((OH)_2UO_2)_n^{+2}$, $Al((OH)_3Al)_n^{+3}$ (in acid solution), $OH((OH)_3Al)_n^{-1}$ (in alkaline solution), and $Th((OH)_3Th)_n^{4+n}$. The hydrolysis of Fe(III) and Bi(III) are treated in sufficient detail to obtain equilibrium constants. For Fe (III) only a small amount of mononucleate product is said to be present, the main reaction being:

$$2Fe^{+3} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{+4} + 2H^+ \qquad \log K = -2.8$$

For the hydrolysis of Bi(III) ion, two hydrolysis constants were determined:

$$2Bi^{+3} + 2H_2O \rightleftharpoons Bi_2(OH)_2^{+4} + 2H^+ \qquad K = 0.010$$

$$Bi_2(OH)_2^{+4} + 2H_2O + Bi^{+3} \rightleftharpoons Bi(OH)_2Bi_2^{+5} + 2H^+ \qquad K = 0.48$$

Hietanen (69) extended the "core plus links" interpretation to hydrolysis of Th(IV), and found that the data can be interpreted by writing all complexes in the form $Th((OH)_3TH)_n^{4+n}$ with a wide distribution of n values from 1 to more than 6. The experimental results could be approximated by assuming that the equilibrium constants for the successive steps are the same.

$$Th((OH)_3Th)_n^{4+n} + Th^{+4} + 3H_2O \rightleftharpoons Th((OH)_3Th)_{n+1}^{5+n} + 3H^+$$

with $\log K = -7.50$. A chain-like structure was suggested. The authors report excellent agreement with the measurements of Kraus & Holmberg (70), although there is a difference in the interpretation of the results. The hydrolysis of other tetravalent ions, notably those of Hf(IV) and Zr(IV), have been previously investigated by Connick & Reas (71) and general equations were developed for interpreting the data on the basis of the formation of a distribution of polynucleate forms.

Polynucleate structures of the type described above are not usually considered to be metal chelate compounds, although chelate rings are undoubtedly present. It is possible, however, that the specific models proposed by Sillén (66) may be useful in the field of polynucleate metal chelates and complexes, for which the number of possible structures is greatly reduced by the blocking of some of the coordination positions in the aquo metal ion by the ligand.

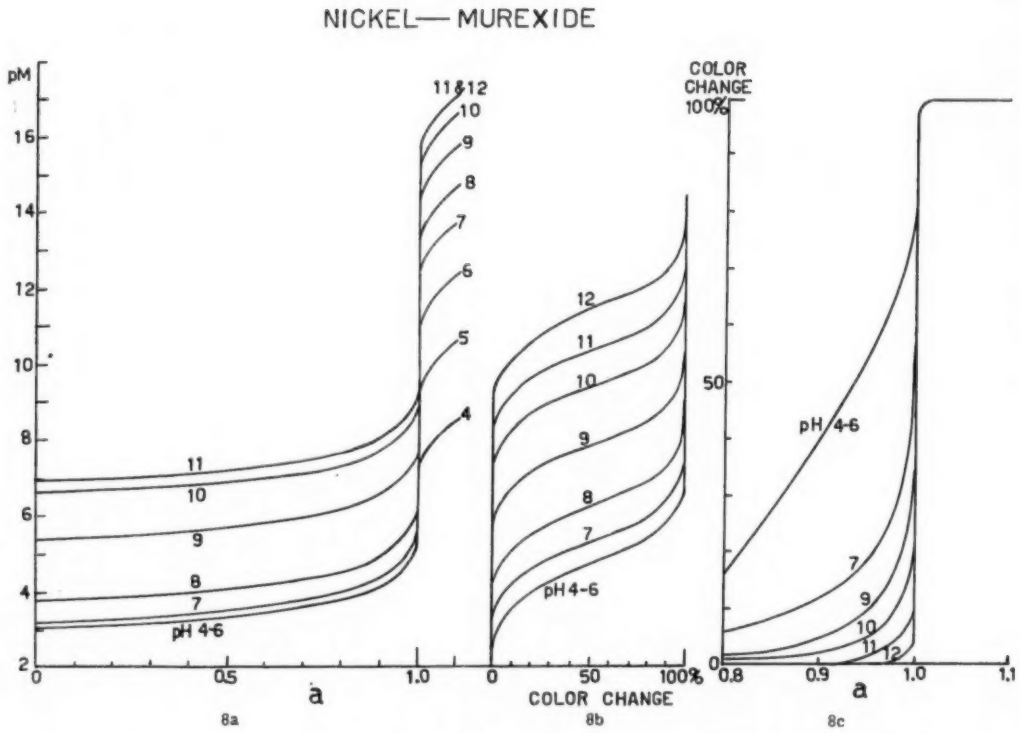

FIG. 8. pM–pH relationships in Ni(II)–EDTA–murexide systems; a = moles EDTA present per mole of Ni(II) salt.

Metal titrations.—Although the greatest activity in the field of metal chelate compounds has occurred in the application of equilibrium data to quantitative analysis of metals, this subject is reviewed by Schwarzenbach (72) in a book soon to be published and will not be discussed in detail here. Figure 8 illustrates how "concentration constants" and the concept of pM and metal buffer systems may be employed in metal titrations. Figure 8a indicates the influence of added ligand on pNi (the negative logarithm of $[Ni^{+2}]$) at various pH levels, while Figure 8b shows the indicator color change as a function of pNi at the same pH values. Both 8a and 8b may be obtained directly from the acid dissociation constants and metal chelate formation constants of the ligand (EDTA) and the dye (murexide). Combination of the curves in 8a and 8b gives the curves in Fig. 8c, which defines the conditions for the quantitative titration of Ni(II) with murexide indicator and a standard solution of a salt of EDTA.

Other subjects.—Space limitations do not allow a discussion of, or even the inclusion of a list of recently-published stability constants. However, a complete compilation of such data published through the end of 1953 is being prepared for publication by the Subcommission on Stability Constants of Complexes of the Analytical Section of the International Union of Pure and Applied Chemistry. It is also not possible to discuss in in this review such interesting topics as metal buffers, and the results of infrared spectra, dipole moments, and magnetic resonance measurements on metal chelate compounds. However, developments in these fields are just beginning and it would perhaps be better to wait until later before a review is attempted.

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EXPERIMENTAL MOLECULAR STRUCTURE AND CRYSTALLOGRAPHY[1]

By Edward W. Hughes

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As in all recent years, the huge volume of papers published in this general field forces the reviewer to pass over many interesting and valuable researches and to attempt to select for review either those which are in themselves particularly noteworthy or those which, in conjunction with others, serve to outline some particular trend within the field. Almost without exception, papers of an experimental nature have not been mentioned unless they present a fairly complete and reasonably reliable determination of the structure of either a crystalline material or of a gas molecule, or present a significant improvement in the accuracy of an older determination.

In the previous year's review, Professor Cox made an extensive list of the reference literature of crystallography. One may now add to his list Volume 13 of *Structure Reports* (1) covering 1950, and one must note the revival of the *Zeitschrift für Krystallographie*, which suspended publication in the latter months of the war. The first of the new issues, Volume 106, No. 2, released late in 1954, contained no structure papers suitable for review here.

In July of 1954 the International Union of Crystallography held its third General Assembly and International Congress at Paris. About 630 crystallographers were in attendance and about 350 papers were on the program. Abstracts have been published (2) but these have been covered below only in exceptional cases, usually where the work has been published in detail elsewhere. The Congress was particularly noteworthy because it was the first to be attended by a Russian delegation. Members of the delegation presented to interested crystallographers a bound collection of papers on crystallographic subjects, each in Russian and in French, prepared specially for the Congress (3). The new President of the Union is R. W. G. Wyckoff and the Fourth Congress is scheduled for 1957 at Montreal.

Methods

There has been considerable activity in Russia in the investigation of crystal structures by electron diffraction. Pinsker (4) has given a general discussion of the method and some of the results are reviewed below. Because the scattering factor curves for electrons are frequently so different in shape and magnitude from those for x-rays, it is sometimes possible to resolve atoms by electron diffraction which can be differentiated only with difficulty by x-ray diffraction; the outstanding example is, of course, hydrogen, which can be located quite well in organic crystals.

[1] The survey of the literature pertaining to this review was concluded on January 15, 1955.

Interest has continued in the scattering factors themselves. Qurashi (5) has computed and tabulated the factors for scandium, titanium, and vanadium, thus filling in the table of Viervoll & Ögrim (6). Ibers & Hoerni have computed and tabulated scattering curves for both electrons (7) and x-rays (8). For the latter, they have used Hartree-Fock radial wave functions but have made the calculation only for carbon, nitrogen, and oxygen. The results are in good agreement with those of McWeeny (9) and confirm that earlier values are significantly in error for some ranges of sin θ/λ.

An experimental technique which may alter greatly the design of x-ray diffraction equipment has been suggested by Weiss, DeMarco & Weremchuk (10). They propose the use of fluorescent x-rays for preparing powder diagrams and have tested the idea by revising a commercial fluorescent analysis instrument. Instead of using a known crystal to examine rays from an unknown fluorescing source they substitute a pure, known fluorescent source, separate the K_β line with a filter, and study the diffraction pattern produced by a powder sample. The major advantages are (*a*) negligible background, and (*b*) complete freedom in choice of radiation. One might add that this choice does not entail the purchase of an expensive x-ray tube for each new choice; any fluorescent source is excited by rays from the same high-powered tungsten target tube. The major disadvantage expected is a reduction in intensity. In the test cited the intensity of the final pattern was no less than half that obtained from the same sample in an ordinary diffractometer designed by the same manufacturer responsible for the fluorescent spectrograph, and the tungsten tube used in the latter was by no means the most powerful on the market. This intensity claim was hotly disputed by representatives of equipment manufacturers when this work was presented before the April, 1954, meeting of the American Crystallographic Association and it remains to be seen how well the authors' claims can be translated into a satisfactory commercial instrument.

A great controversy has developed during the year over the method proposed by Karle & Hauptman for the solution of the phase problem in x-ray crystallography. Although they first described their method at the June, 1953, meeting of the American Crystallographic Association, and their monograph (11) is dated September, 1953, the details of the method did not become generally distributed until 1954. They have published more in past months (12, 13), and Christ, Clark & Evans (14) have described an application of the method in solving the structure of the mineral colemanite. The method has been severely criticized; the principal published attacks are by Vand & Pepinsky (15, 16) and Cochran & Woolfson (17). The method is statistical in nature. Distribution functions are derived which show the distribution of the magnitude of a group of structure factors when the values of certain related structure factors are known. The distribution functions are not obtained in closed form and to facilitate computations approximations are made by neglecting terms of the expansion involving higher powers of the variates. Relationships result which permit one to calculate the proba-

bility that a certain structure factor has a certain sign when certain other related structure factors have their observed magnitudes. Some relations require that these latter related structure factors be of known sign, but others do not. The probability is often very nearly equal to one-half (i.e., plus or minus equally probable) particularly in complicated structures, but the authors assert that by involving the same structure factor in a large number of such relations systematically and combining the results, the sign probability can be made as near to unity as desired. The critics deny this. They point out that the summations over the structure factors which are involved are precisely like those evaluated in the mathematical operation of convolution and the resulting magnitudes and signs are the coefficients of Fourier series of predictable nature and that the latter are, in general, never the true structure. In particular, the relation relied upon at the start when no signs are known gives, for example in $P\bar{1}$, the coefficients of the square of the sharpened Patterson function with the peak at the origin removed. If these signs are then applied to the proper structure factor magnitudes they cannot yield the actual structure unless the Patterson happens to look very much like the structure itself, a very unlikely circumstance. Karle and Hauptman, as a test, computed correct signs for a small group of structure factors from the measurements on naphthalene, not in itself a difficult test substance. Vand and Pepinsky show that these data correspond to a section in Patterson space which does, in fact, happen to resemble the corresponding section in real space and they attribute this success to this resemblance. Christ & co-workers have correctly solved the colemanite ($CaB_3O_4(OH)_3 \cdot H_2O$) structure by applying the Karle-Hauptman process to three-dimensional data. This is a moderately complex crystal but unfortunately the x-ray scattering is dominated by the calcium present to such an extent that the problem is nearly a "one-atom" example and could be solved more easily by Patterson projections. The details of the structure have not been given but from the published projection the reviewer notes that the calcium parameters in the x and z directions are such that the Patterson projection does again look like the structure projection and so one must expect the method to give correct signs at least for $h0l$ structure factors. If, as seems likely from the published drawing, the calcium y parameter is approximately $\frac{1}{4}$ or $\frac{3}{4}$, the entire "calcium" Patterson will resemble the calcium Fourier and the successful operation of the method is compatible with the criticisms given. On the other hand, the reviewer knows of no clear test, satisfactory to all, in which the method has been shown to have failed. The trivial example cited by Vand & Pepinsky is a very tricky one with linear integral relationships between the atomic parameters and such relations have been specifically ruled out by Karle and Hauptman. Although it is only a four-atom cell with large unitary structure factors and one would expect to solve it easily with inequalities, one can, in fact, find signs for only three out of sixty-three structure factors using the first Harker-Kasper inequality. Accordingly, the experimental decision regarding the worth of this method must await the

completion of efforts now under way. On theoretical grounds many crystallographers seem inclined to doubt that the method really is the solution of the phase problems.

One of the Karle-Hauptman results is identical with the "sign product" relationship already discussed by Sayre, Cochran and others and used by Zachariasen in outlining a method for solving structures when the signs of a few large structure factors are known. The convolution involved in this relationship leads to signs for the square of the structure rather than to some function of the Patterson, and accordingly it is not surprising that it yields correct results, particularly when applied to structures where all atoms are nearly alike in scattering power. Even when the atoms are not alike, if the heavier ones dominate the scattering the same result holds. Interest in this relationship has continued during 1954. Kitaĭgorodski (18) has discussed the probability that the product $U_H \cdot U_K \cdot U_{H+K}$ is positive and has outlined a procedure for applying his results. Rumanova (19) has described her application of Zachariasen's method. Bertaut & Pepinsky (20) have discussed the conditions under which Zachariasen's method will work but it must be noted that their relationship (12b in their paper), $S_H \approx -S(\overline{S_K S_{H-K}})$, was not proposed by Zachariasen and is not true. Woolfson (21) has given an alternative discussion of the problem treated by Kitaĭgorodski and has shown that actual data from crystals conform to the statistics proposed.

New sign-determining methods have been proposed by Cochran (22), and Vand (23) and Vand & Pepinsky (16) have proposed modifications of the Karle-Hauptman method. At the moment, nothing is known of the practical value of these works except that Cochran has stated that the auxiliary conditions required for his method to hold are so restrictive that it will rarely be useful except for the simplest crystals.

Mineral Structures

The structure of epidote appears to be settled at last. Ito, Morimoto & Sadanaga (24) have published the details of their three-dimensional refinement. There are no corrections for series termination effects, which must be considerable, and the over-all R is 27.5 per cent. But there can be no doubt of the essential correctness of the structure. If there were doubts they would be dispelled by the excellent agreement with the independent results reported by Bélov & Rumanova (25). The methods used by the latter are not stated in the abstract available but the two sets of parameters agree on the average to a few thousandths of a cell edge. The structure contains both SiO_4^{-4} and $Si_2O_7^{-6}$ groups, bound together by calcium, iron, and aluminum ions. There is one OH^- and one O^{-2} not linked to silicon. The formula is thus $Ca_2FeAl_2O(OH)Si_2O_7SiO_4$, with some isomorphous replacement of iron by aluminum.

Contradictory results are reported for another important silicate, nepheline. Buerger, Klein & Donnay (26) give a preliminary structure based on $P6_3$ with 8 $NaAlSiO_4$ per cell while Bélov (27) reports a structure based on

$P\bar{3}c$ with 2 $Na_4Al_4Si_5O_{18}$ in a cell of substantially the same size. On the basis of x-ray evidence presented, the former structure seems much more probable but will need considerable refinement before it can be accepted as final. It is derived from tridymite by replacing half of the Si atoms by Al atoms and balancing the charges by inserting Na^+ ions in holes available in the tridymite structure. As some of the holes are larger than others, the tendency to take a certain proportion of K^+ ions instead of Na^+ is explained.

Other interesting mineral structures which cannot be described here are those of magnesium vermiculite by Mathieson & Walker (28), and realgar by Tobelko, Zvonkova & Zhdanov (29).

Inorganic Structures

There are eight papers dealing with the stereochemistry of sulphur, selenium, and tellurium. Ohlberg & Vaughan (30) report on the crystals of selenium dithiocyanate while Aksne & Foss (31) have investigated the isomorphous crystal selenium diselenocyanate. Each molecule has a mirror plane passing through its central selenium atom and the bond lengths and angles appear about normal, with the exception that the dihedral angle in the thiocyanate, only 79°, is small. A set of closely related works report on (*a*) barium tetrathionate dihydrate [Foss, Furberg & Zachariasen (32)]; (*b*) barium pentathionate dihydrate [Foss, & Zachariasen (33)]; (*c*) ammonium telluropentathionate [Foss & Larssen (34)]; (*d*) selenium dibenzene sulphinate [Furberg & Öyum (35)]; and (*e*) tellurium dimethane thiosulphonate [Foss & Vihovde (36)]. The pertinent groups have these structures:

(*a*) $(-S-SO_3)_2^{-2}$ (*b*) $S(-S-SO_3)_2^{-2}$ (*c*) $Te(-S-SO_3)_2^{-2}$ (*d*) $Se(-SO_2-\phi)_2$
(*e*) $Te(-S-SO_2-CH_3)_2$

All of these groups show the expected bond angles and the dihedral angles range from 81° to 110°. The average distances are: S–O, 1.42 Å; S–Te, 2.35 Å; S–Se, 2.20 Å; S–C, 1.79 Å. The S–S distances fall into two groups, one averaging 2.13 Å, the other 2.03 Å. The short ones always fall at the center of chains [(*a*) and (*b*) above] but it is not at all certain that the difference exceeds possible error; it has been shown in the past year [see geranylamine hydrochloride, (67) below] that failure to allow for varying temperature factors in chain compounds can produce errors of this magnitude. Abrahams (37) finds two distances also in the S_4^{-2} ion in $BaS_4 \cdot H_2O$ but the two distances, averaged from two nonequivalent S_4^{-2} ions in the structure, are 2.026 Å and 2.067 Å and as these differ by only the estimated standard deviation for a single determination the discrepancy is hardly significant. The dihedral angles are 74°5′ and 77°10′ and these, in conjunction with the values from CsS_6, are said to establish a value of about 76° for sulphur chains. But the works reviewed immediately above show values of 102°, 104°, and 110° in sulphur chains so we must conclude that the dihedral angle depends sharply upon circumstances.

Work continues on the boron hydrides. Lipscomb (38) has reviewed

earlier experimental results, and Lavine & Lipscomb (39) have published the crystal structure of B_5H_{11} as determined at $-140°C$. The boron arrangement corresponds to a tetragonal pyramid distorted by stretching one edge of the tetragonal base until the borons at the ends of this edge are too far apart to be considered as bonded. The hydrogens are arranged as in B_5H_9 except at the stretched edge, where the bridge hydrogen of that edge in B_5H_9 is now replaced by three hydrogens, each singly bound to one of the three nearest borons, two in the base and one at the apex of the distorted pyramid. The bond lengths are, within experimental error, consistent with values from other boron hydrides.

Sulphur trioxide and its compounds with N_2O_5 and HNO_3 have been reported [Westrik & MacGillavry (40); Eriks & MacGillavry (41); Steeman & MacGillavry (42)]. The asbestos-like form of SO_3 (β-form) contains endless chains —O—SO_2—O—SO_2— consisting of SO_4 tetrahedra sharing corners. The S–O distances in the chain (1.61 Å ave.) are significantly larger than those to side oxygens (1.41 Å ave.). The same distances occur in the γ-form which contains closed rings of linked tetrahedra. The endless chain has a twofold screw axis. The oxygen atoms are in cubic close packing, slightly deformed by the bonds to sulphur, and a single $(SO_3)_n$ chain resembles a column cut from the zincblende-type structure. The compound $N_2O_5 \cdot 3SO_3$ is shown to be ionic, the ions being NO_2^+ and $S_3O_{10}^{-2}$, and similarly $HNO_3 \cdot 2SO_3$ is made up of NO_2^+ and $HS_2O_7^-$. The negative ions are made up of SO_4 tetrahedra sharing corners to form unbranched chains. The distances have not been determined with precision but are all reasonable.

Havinga, Boswijk & Wiebenga (43) have shown that in crystalline CsI_4 the iodine exists in a complicated arrangement which consists of I_3^- ions and I_2 molecules bound together by weak bonds to form a structural unit $(I_3—I_2—I_3)^{-2}$ which is nearly planar, but not linear; the I_2 is nearly perpendicular to the two I_3 groups, which are related by a center of symmetry in the I_2 group. The I—I distance between I_2 and I_3 is 3.42 Å compared to a minimum distance of 3.9 Å between different I_8^{-2} groups. The I_3 group is not symmetrical, the two distances being 2.84 Å and 3.00 Å. Boswijk & Wiebenga (44) have found that ICl_3 is built of planar I_2Cl_6 molecules although the intermolecular Cl—Cl distances (3.57 Å ave.) are substantially the same as those inside the I_2Cl_6 group, which is made up of two nearly square ICl_4 groups sharing an edge. The I–Cl bonds to the shared chlorines average 2.70 Å, very much longer than the other I–Cl bonds which average 2.385 Å. These "molecules" form layers; the distance between layers is only 3.42 Å but the shortest Cl—Cl between layers is 3.68 Å, about the same as inside a layer.

Zhdanov & Rusakov (45) have reported a number of structures isomorphous, or nearly so, with pseudobrookite, Fe_2TiO_5. The substances now described are Al_2TiO_5, Ti_2MgO_5 and a new oxide of titanium, Ti_3O_5. The latter was first found in blast furnace slag but the x-ray analysis was carried out with synthetic material. All of the metal ions are in octahedral coordina-

tion but whereas one is in a fourfold position with symmetry *mm* the other two are in one eightfold position with symmetry *m* and must be the same. As shown by this work one can have a tetravalent ion in the first position and a trivalent ion in the second (Fe_2TiO_5, Al_2TiO_5) or, instead, a bivalent ion in the first position and a tetravalent ion in the second (Ti_2MgO_5). In the Ti_3O_5, one-third of the titaniums must be tetravalent and the others trivalent. The substance, as seems generally to be true when two valences of the same element occur together, is so absorbing optically as to appear jet black.

Zachariasen (46) has refined the structure of orthoboric acid with Geiger counter intensity measurements and has made a novel use of a generalized projection to obtain accurate values of the coordinates in the direction of projection. The hydrogens were located by a generalized difference projection. The six nonequivalent B–O distances (two nonequivalent H_3BO_3 per cell) average 1.361 Å and lie between 1.353 Å and 1.365 Å. For the six O–H—O bonds the average is 2.72 Å (2.707 Å to 2.734 Å). The layers are nearly but not exactly planar.

Siemons & Templeton (47) have investigated at low temperature the hydrate of ammonia, $2NH_3 \cdot H_2O$. This is a rather open structure. One of the ammonias and the water form a three-dimensional network held together with hydrogen bonds, the bond lengths being between 2.84 Å and 3.22 Å. All nonbonded approaches are greater than 3.6 Å. The second ammonia is linked by a single hydrogen bond of length 2.85 Å to waters of the framework.

The structure of β-uranium continues in doubt. Thewlis & Steeple (48) have proposed a new structure but Tucker (49) has given arguments to show that, so far as agreement with the intensity data is concerned, there is no choice to be made between it and that put forward by himself.

Hassel & Hvoslef (50) have investigated an addition compound of dioxane with elementary bromine. The Br–Br distance is 2.31 Å (gas value 2.28 Å), and the Br_2 molecules form bridges between oxygen atoms of two different dioxane molecules: —OC_4H_8O—Br–Br—OC_4H_8O—. The Br—O distances are 2.71 Å, considerably less than the van der Waals radii sum.

Edstrand & Ingri (51) find that the oxygen in $LiSbO_3$ is in distorted hexagonal close packing with Li and Sb occupying octahedral holes. Although the Sb octahedra share edges to make staggered chains running through the crystal it seems more appropriate to call the substance a double oxide rather than an antimonate.

Harvey & Bauer (52) have made an electron diffraction study of the vapor of a compound of empirical formula $S_2F_{10}O_2$ and although the number of parameters is large for a completely independent determination, by assuming some symmetry in some groups to simplify the determination they have demonstrated with considerable certainty that the structure is a peroxide, F_5S–O–O–SF_5. Sulphur is in octahedral coordination between five fluorines and one oxygen. The dihedral angle —S—O—O—S— is 107°, about the same as in hydrogen peroxide. The O–O bond, 1.46 Å, is also normal and

likewise the S–O length of 1.67 Å. The S–F value of 1.56 Å is somewhat less than the radii table sum but is about the same as is found in SF_6.

Bond & Brockway (53) have completed a similar investigation of the mono-, di- and trimethyl derivatives of silane. The C–H bonds are 1.09 ± 0.02 Å and the Si–H bonds are 1.48 ± 0.02 Å. The Si–C bond length decreases steadily with the increasing number of methyls substituted but the total change exceeds only slightly the sum of the possible errors: 1.873 ± 0.006, 1.860 ± 0.004, and 1.857 ± 0.007 Å in the mono-, di- and trimethyl derivatives, respectively. The bond angles are all close to the tetrahedral value.

Badgley & Livingston (54) have made a new electron diffraction study of $POCl_3$ vapor and find new parameters in excellent agreement with microwave results. They report P–Cl, 1.995 ± 0.02 Å; P–O, 1.45 ± 0.05 Å; $\angle$ ClPCl, $103.5 \pm 1°$.

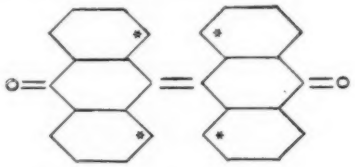
Bowen has investigated a number of compounds involving the trifluormethyl radical, using gaseous electron diffraction. For the trifluormethyl halides (55) his work checks well with an earlier investigation. New results include trifluormethyl derivatives of Group VI elements (56) and of Group V elements (57). In all of these the C–F bond ranges from 1.326 Å to 1.356 Å, none being significantly different from their average, 1.337 Å, which agrees with the values obtained in the most recent investigations of fluorocarbons. In $S(CF_3)_2$, $S_2(CF_3)_2$, and $S_3(CF_3)_2$ the S–C average is 1.835 Å and the S–S average is 2.06 Å. In $Se(CF_3)_2$ and $Se_2(CF_3)_2$ the Se–C average is 1.946 Å and Se–Se is 2.335 Å. From $P(CF_3)_3$, $As(CF_3)_3$ and $Sb(CF_3)_3$ the results show: P–C, 1.937 Å; As–C, 2.053 Å; Sb–C, 2.202 Å. These are normal, within experimental error, except for P–C and As–C, which exceed expected values by more than the estimated error.

In this review of inorganic structure investigations, no effort has been made to cover the voluminous work on metals and alloys. Only a few of a possible 20 or more examples of double salts or complex coordination type compounds have been described.

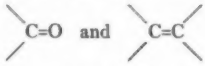
Organic Structures

There has been much work done during 1954 on molecules which have been described as "overcrowded." These are molecules which by ordinary stereochemical principles would be expected to have a configuration which would bring two or more nonbonded atoms of the molecule closer together than is allowable by the minimum van der Waals radii; the repulsion between these atoms forces the balance of the molecule to take on a configuration contrary to expectation. As a classical example one might cite the case of *cis*-azobenzene where the molecule, which one otherwise would expect to be planar, is forced into a nonplanar configuration by the repulsion of the phenyl groups. Four papers have appeared by Schmidt and associates. In Part I [Harnik *et al.* (58)] they record a survey of the subject and unit cell and space group determinations for nineteen different crystals. The remain-

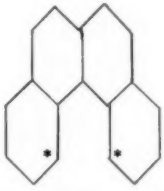
ing Parts, II, III and IV, describe three substances in detail. Harnik & Schmidt (59) describe dianthranylidene,



This molecule one would expect to be planar if it were not for repulsion between the starred atoms where, in a planar molecule, there would be CH—CH separations of less than 1.5 Å. The central doubly-bonded group is planar as are also the atoms attached to the carbonyl carbons. But the end benzene rings of the anthracene skeletons are bent up and down sufficiently to make the CH—HC distance 2.9 Å. The C–C bonds adjacent to

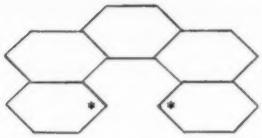


are practically single bonds, the lengths running from 1.51 Å to 1.54 Å. The C=C itself is 1.31 Å, a pure double bond. Herbstein & Schmidt (60) have investigated 3:4 benzophenanthrene:



Here in a flat molecule there would be a CH—CH distance of about 2.4 Å between starred atoms, too small to be tolerated. One of the terminal benzene rings is bent up, the other down, and the observed CH—CH distance is 3.00 Å. The distortion is distributed over the whole molecule. The central C–C bond, at the junction of the two naphthalene residues, has a length 1.55 Å and must, therefore, be practically a single bond. One other C–C bond is as high as 1.47 Å and another is as low as 1.32 Å. Although the accuracy of the determination is not high these variations appear to be outside experimental error. Herbstein & Schmidt (61) have also given an account of preliminary work on tetrabenzonaphthalene. Although the analysis is not complete it is established that the molecule is not planar.

McIntosh, Robertson & Vand (62) have published the final details of their work on 3:4–5:6 dibenzophenanthrene, the first "overcrowded" structure to be investigated, and where the repulsion is severe:



The distance between starred atoms would be about 1.4 Å in a planar molecule. The observed value is 3.00 Å, averaged for two nonequivalent molecules in the unit cell. One of these molecules is located on a twofold axis which passes through the edges of the central benzene ring. The distortion is distributed over the whole ring system in such a way that individual bond lengths and angles do not seem greatly disturbed.

Finally, Nyburg (63) has made a three-dimensional analysis of the data of Fenimore (64) from dibiphenylene-ethylene. Here there are two CH—CH approaches which would be about 2.5 Å in a planar molecule. As a result of two-dimensional analysis, Fenimore proposed such a planar structure. Nyburg finds that the molecules are not planar and as he finds the same configuration for two crystallographically nonequivalent molecules in the cell, there is little doubt that even this relatively small compression of the van der Waals radii is not to be tolerated.

Russian workers have described the location of hydrogen atoms by electron diffraction of substances previously examined by x-rays. Weinstein (65) has made a three-dimensional study of diketopiperazine, first reported by Corey in 1938 (66) on the basis of two-dimensional x-ray data. Although the electron diffraction data do not extend to such high orders as Corey's data do, the fact that they are three-dimensional and the relative magnitudes of the scattering powers of C, N, O, and H for electrons permit the location of the hydrogen atoms. Because Corey reported a C–C bond of only 1.47 Å and C–N bond of only 1.41 Å, and because of the two-dimensional nature of his work, there has been some question regarding the reliability of these bond lengths. Weinstein does not state what corrections, if any, were made to his series for termination errors nor does he say how he has computed his mean square errors, so it is not clear how much trust may be given them. But it is interesting to see how closely he confirms Corey's values:

	C–C	C–N	C=N	C=O
Weinstein:	1.44	1.40	1.38	1.22 Å
Corey:	1.47	1.41	1.33	1.25 Å

Corey's two low values are given even lower by Weinstein. The latter also gives C–H, 1.11 and 1.09 Å and N–H, 0.98 Å. The latter hydrogen is involved in a hydrogen bond to an oxygen of a neighboring molecule. The stated errors (r.m.s.) are ± 0.012 Å for heavy atom bonds and ± 0.031 Å for bonds to hydrogen. The electron diffraction photographs are made from thin polycrystalline films which, if possible, have had the crystallites oriented parallel to each other. Weinstein attributes small deviations between the x-ray and electron cell constants to distortions due to surface effects in his

very small crystallites. But as the discrepancies are all less than a per cent one can easily doubt their significance.

A result of great importance has come out of a recalculation of the structure of geranylamine hydrochloride by Cruickshank & Jeffrey (67). The original work indicated an abnormally short C–C bond of only 1.44 Å between two isoprene units. In the new calculation, performed on the Manchester University electronic computer, four cycles of differential syntheses were carried out with separate temperature factors for each atom. Inspection of the Fourier syntheses of the earlier work suggested strongly that atoms near the ionically bound sheets of Cl^- ions and NH_3^+-CH_2 groups undergo smaller temperature vibrations than the carbon atoms near the ends of the chains, where only van der Waals forces operate. In the new analysis this is confirmed and the temperature factors increase steadily along the chain as one progresses from ionic to van der Waals binding. The important result is that when the structure is refined in this way, the "abnormal" C–C length has increased to 1.537 Å with a standard deviation of 0.045 Å so that there is no longer any significant shortening from the usual single bond value. But despite these considerable shifts in atomic positions, the isoprene groups remain planar. This investigation casts doubt on all previous work where different atoms have obviously different temperature vibrations which have not been taken into account with separate atomic temperature factors.

An example where the introduction of separate temperature factors did not produce marked changes in interatomic distances is afforded by the preliminary report on parabanic acid by Davies & Blum (68). This planar molecule, $H_2C_3O_3N_2$, can be considered as the ureide of oxalic acid. One expects it to have symmetry *mm* and although it actually is in a general position with no crystallographic symmetry, the molecule found does come remarkably close to the expected symmetry. As the Fourier syntheses suggested anisotropic temperature vibrations, separate anisotropic temperature factors were introduced for each atom. Although this type of refinement reduced the *R* factor considerably it produced only minor changes in the atomic coordinates. The agreement between chemically equivalent bond lengths is outstanding: C–N, 1.379 and 1.381 Å; C–N, 1.358 and 1.358 Å; C=O, 1.214 and 1.208 Å. The other two distances, which occur only once each, are: C=O, 1.210 Å; C–C, 1.541 Å. The latter corresponds to the famous controversial C–C length in oxalic acid dihydrate. So, even here, where this distance is incorporated into a heterocyclic ring it remains of normal length. The standard deviations for the above values are all about ± 0.003 Å.

Cox & Smith (69) have published a preliminary report of their reinvestigation of solid benzene at $-3°$C. From three-dimensional studies they have found the three crystallographically nonequivalent distances to be: C–C, 1.377, 1.382, and 1.374 Å, mean 1.378 Å with a standard deviation of ± 0.0033 Å. However, this appears to be significantly different from the Raman spectra value 1.396 to 1.401 Å and as there are very probably anisotropic temperature vibrations, the refinement will be continued with separate

temperature factors for each atom. The final result will be of great interest, not only in connection with the question raised in the previous two structures, but because the C–C length in benzene is always taken as one of the fixed points on the bond length versus bond order curves for carbon-carbon bonds.

Several structures have appeared which are related to the controversial oxalic acid mentioned above. Ayerst & Duke (70) have completed an unusually careful refinement for oxamide using separate temperature factors. The C–C length is 1.542 ± 0.006 Å; C–O, 1.243 ± 0.004 Å; C–N, 1.315 ± 0.004 Å. The N–H—O bonds which link the planar molecules into sheets are 2.941 and 2.949 Å. Jeffrey & Parry (71) have examined the sodium salt of oxalic acid and find the ion to be planar with C–C, 1.54 Å; C–O, 1.23 Å; ∠C-C-O, 115° and 121°; ∠O-C-O, 124°. Pringle (72) has made Geiger counter measurements of the (*h*0*l*) zone of oxalic acid dihydrate itself and with coordinates from previous work has computed a difference map which shows the hydrogen positions. It is found that hydronium ions do not exist in this substance, the acid hydrogens being still attached to oxalic acid oxygens. This is in agreement with proton magnetic resonance and optical experiments. Long, Markey & Wheatley (73), find in dithio-oxamide the normal C–C bonds, 1.544 and 1.534 Å for the two molecules in the cell. Their C–N lengths, 1.308 and 1.285 Å, are a bit shorter than the corresponding value 1.315 Å quoted above from oxamide. The C–S values are 1.663 and 1.662 Å, corresponding to a large amount of double bond character. The general conclusion to be drawn from all these structures is that there is nothing abnormal in the length of the central C–C bond of oxalic acid and related compounds. All of them now known appear to be planar, even the ionic forms, with the single exception of the oxalate ion in ammonium oxalate. Since the normal C–C distance rules out conjugation across this bond, the most common explanation of this planarity is also ruled out. Whatever other forces tend to keep the two ends of these molecules coplanar are not strong enough to counteract the torsions introduced by the extensive hydrogen binding in the ammonium oxalate.

Fluorene, which was once claimed to be nonplanar [Iball (74)] is now shown to be flat by two independent examinations [Burns & Iball (75) and Brown & Bortner (76)]. Refinement is not yet complete.

Two independent sets of workers, [Vand & Pepinsky (77) and Pinnock & Lipson (78)] have called attention to an error in the structure reported earlier for triphenylene by Klug (79). Klug's structure is built of molecules which are probably of nearly correct configuration and orientation; the error is in the position of the center of the molecule which is displaced from its proper location by more than 1 Å. Yet the *R* ratio for the best resolved zone was claimed to be as low as 0.20. The molecule has all of its atoms near points on a hexagonal net. If the molecule is displaced by the separation between a row of these points there are still many of the correct intermolecular interatomic distances duplicated in the wrong structure, while all the intra-

molecular distances are unchanged. Accordingly, although some signs change, many intensities are almost unaltered, and Vand & Pepinsky had to resort to inspection of intermolecular distances to aid in selecting the proper location of the molecule. These distances are now all found to be greater than 3.60 Å, as compared with Klug's low of 2.58 Å, and there is no evidence of powerful bonding forces between molecules. The new structure is being refined by Pinnock and Lipson.

Ladell & Post (80) have completed a three-dimensional examination of formamide with data collected at −50°C. They find C–O, 1.255 Å; C–N, 1.300 Å; probable error ±0.013 Å. The bond angle at the carbon atom is 121.5°. Molecules related by a center of symmetry are "dimerized" by hydrogen bonds of length 2.935 Å. Each "dimer" is then bound to other "dimers" by four hydrogen bonds of length 2.88 Å. In this way sheets are formed which are separated by van der Waals distances between atoms of 3.39 Å or greater.

Howell, Curtis & Lipscomb (81) have shown that the six-membered ring of 1,4-dithiadiene, $C_4H_4S_2$, is not planar, but is bent along a line joining the two sulphur atoms. They find C–S, 1.78 Å and C–C, 1.29 Å, both ±0.05 Å. These are averages of two bonds each and the actual distances diverge greatly from the averages. The dihedral angle between the two halves of the molecule is about 140°.

An examination of dipotassium nitroacetate by Sutor, Llewellyn & Maslen (82) reveals a planar nitroacetate ion, $(CO_2CHNO_2)^{-2}$. All the bonds are considerably shorter than single bond values because the two double bonds have access to all bonds in the molecule. But for the same reason, the double bond character in the C–O bonds and N–O bonds of the carboxyl and the nitro groups is less than usual and the bonds are longer than is customary in such groups: C–O, 1.27 and 1.33 Å; N–O, 1.26 and 1.28 Å; C–C, 1.38 Å; C–N, 1.39 Å.

Farag (83) has completed the refinement of 1,3,5-triphenylbenzene. This molecule should probably have been included among the "overcrowded" structures for it is nonplanar and the cause appears to be steric hindrance between the edges of adjacent benzene rings. If planar there would be CH—CH distances of about 2.41 Å. The observed values range from 2.90 to 3.00 Å. The three phenyl groups are rotated about their bonds to benzene by 34°, −27°, and 24°, respectively.

Brown (84) finds the structure of 4,4′-dimethyldibenzyl to be very similar to that of dibenzyl itself. The molecule is centrosymmetrical but the two benzene rings are not coplanar. Although the single-bonded C–C distances range from 1.51 to 1.53 Å they cannot be considered significantly short.

Tropolone, $C_7H_6O(OH)$, is an amphoteric substance forming salts with either acids or bases. Sasada, Osaki & Nitta (85) have investigated its salt with HCl. The structure was solved by inequalities. As in tropolone itself, the seven-membered ring is planar with an average C–C distance of 1.40 Å. The two C–O distances are 1.40 and 1.42 Å and we have here an ionic compound $C_7H_6(OH)_2^+$—Cl^-. The molecule is amphoteric because it can gain a

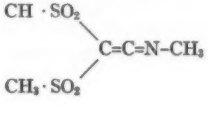
plane of symmetry either by losing a proton from its OH group or by adding a proton to its carbonyl oxygen. The creation of a plane of symmetry by either method increases the number of identical canonical structures available and so tends to increase the resonance stabilization of either kind of ion over that of the neutral molecule.

Speakman has continued his investigation of acid salts of monobasic acids. In potassium acid benzoate, $KH(C_7H_5O_2)_2$, Skinner, Stewart & Speakman (86) find the two benzoate ions crystallographically equivalent, although it must be noted that this result depends upon the statistical test for a center, which sometimes is not reliable. If space group requirements were to hold rigorously the acid proton would be at a center or on a twofold axis and we would be confronted with a symmetrical O—H—O bond. But the observed length of this group is 2.51 Å, corresponding to a strong but unsymmetrical O–H—O bond. The proton must be distributed statistically between the two positions near the oxygens rather than halfway between. Downie & Speakman (87) have solved the structure of ammonium acid salicylate hydrate, $NH_4 \cdot H(C_7H_5O_3)_2H_2O$, and find the salicylate residues are not equivalent crystallographically. The hydrogen bonds are either to water (2.76, 2.65, and 2.65 Å) or are intramolecular, between the hydroxyl and carboxyl oxygen (2.63 and 2.45 Å). The C–O bonds are not determined with sufficient accuracy to aid in establishing the location of the acid proton.

A number of structures have been reported for substances of biological interest. Baily (88) examined an antimalarially active metabolite of paludrine, obtaining the signs by comparing reflections from the isomorphous hydrochloride and hydrobromide. From the resulting projections the material, of empirical formula $C_{11}H_{14}N_5Cl \cdot HCl$, was shown to be the hydrochloride of 4,6-diamino-l-*p*-chlorophenyl-1,2-dihydro-2,2-dimethyl-1,3,5-triazine. The detailed configuration of the molecule was established. Phillips (89) has worked out the hydrochloride of ephedrine and although the chemical structure of this molecule was well-known before, the x-ray work has confirmed the configuration of the structure. Visser, Manassen & deVries (90) examined the hydrobromide of tropine by the heavy atom method. Although chemical methods pretty well established the *trans* configuration before this work was finished the x-ray result not only confirmed the *trans* form but showed that the six-membered ring is in the chair form, at least in the solid state. Fridrichsons & Mathieson (91) undertook the formidable task of attempting to identify an alkaloid, cryptopleurine, for which they knew only the empirical formula and the presence of three methoxy groups. The work utilized the heavy atom technique. A methiodide derivative, boiled in water to form a related racemate, *dl*-isocryptopleurine, was actually solved. The empirical formula involved was $C_{25}H_{30}O_3NI$. The parent substance (i.e., not counting the methiodide group) was shown to be 2,3,6-trimethoxyphenanthro(9,10-b)quinolizidine. Mendel & Hodgkin (92) and Jensen (93) have determined the structure of creatine monohydrate. The two results are in good agreement. The molecule is a zwitterion: $+(NH_2)_2{\equiv}C\text{-}NCH_3CH_2$

CO_2^-. The substituted guanidine group is planar as is also the carboxyl group. The two planes make an angle of 84.5° with each other. The distances and bond angles are all normal. Parry (94) has examined uracil, one of the pyrimidine bases obtained by hydrolysis of nucleic acids. The molecule is planar and in the six membered ring two different C–N distances are found; those associated with one nitrogen are 1.341 and 1.344 Å; those associated with the other nitrogen are 1.374 and 1.384 Å. These two groups appear to be significantly different, the probable errors being about ±0.007 Å. The six-membered ring is like that in adenine (except for substituents) where a similar discrepancy was found. One new amino acid and two dipeptides have been reported. Trommel & Bijvoet (95) have examined the hydrochloride and hydrobromide of D-isoleucine by the isomorphous replacement technique and the heavy atom technique. Their final results show that the crystals are not exactly isomorphous but the heavy atoms and a portion of the amino acid ion are nearly enough alike in position to have led to a correct trial structure. The amino group and the methyl group of the side chain are *cis* to each other and so D-isoleucine is D-α-amino-D-β-methyl valeric acid. All distances are normal, within experimental error, except perhaps the C–N distances of 1.43 and 1.45 Å (chloride and bromide, respectively). These have generally been about 1.49 Å in amino acids in zwitterion form. By using $UL\alpha_1$ rays to excite the Br K electrons, photographs of the hydrobromide, interpreted by the well-known method devised by Bijvoet, showed that the absolute configuration of the asymmetric carbon atoms agrees with the chemical convention. Yakel & Hughes (96) have examined N,N′-diglycyl-L-cystine dihydrate, the first dipeptide solved which contains the important disulphide bridge. The $-CH_2-S-S-CH_2-$group sits on a twofold axis and joins the two dipeptide chains. The S–S bond is 2.04 Å, the S-S-C angle is 103° and the dihedral angle is 101°. These are normal values. The S–C bond of 1.87 Å is significantly longer than the table radii sum. Unlike β-glycylglycine, where the dipeptide chain was planar, except for the terminal NH_3^+ group, we find in this molecule that the plane of the peptide group and the plane of the carboxyl group make a dihedral angle with each other of 19°. Pasternak, Katz & Corey (97) have investigated another dipeptide, glycyl-L-asparagine. Asparagine itself has not had its structure determined by x-rays. They find that the carboxyl group, the peptide group and the terminal amide group of the asparagine side chain are all separately planar. The carboxyl and amide group planes are nearly coplanar and they make an angle of 85° with the plane of the peptide group. Bond lengths and angles agree with corresponding quantities from other peptides and amino acids.

Wheatley (98) has made in N-methyl-2,2-dimethylsulphonylvinylidineamine



the unexpected discovery that the $\diagdown$ $C{=}C{=}N{-}CH_3$ $\diagup$ group is entirely linear and that the bond lengths to the central carbon atom are such as to indicate a bond number considerably greater than four. The bond values are: C=C, 1.342 Å; C=N, 1.154 Å; N–C, 1.426 Å, all about ±0.008 Å, s.d. Separate temperature factors were used for each atom in the refinement and other distances in the molecule are as expected. It is thus very difficult to ascribe these values to error. Similar compounds are being investigated and until these results are duplicated he does not care to speculate regarding the bonding in this chain.

Two compounds involving oxygen in heterocyclic rings are furoic acid [Goodwin & Thomson (99)] and ethylene carbonate [Brown (100)]. Furoic acid, or furane-α-carboxylic acid, is a five-membered unsaturated ring containing one oxygen, and an attached carboxyl group. The C–O bonds in the ring are 1.30 and 1.31 Å while the C–C bonds are: 1.30, 1.46, and 1.35 Å. The C–C to the carboxyl is 1.47 Å and the two C–O values of the carboxyl are 1.16 and 1.26 Å, the latter being undoubtedly to the hydroxyl oxygen. The C–C ring bond lengths indicate that the two double bonds are fairly well localized. In ethylene carbonate the five-membered ring is not planar but the molecule does possess a twofold axis passing through the carbonyl group and the center of the C–C bond opposite it in the ring. The C–C bond makes an angle of 20° with the plane of the CO_3 group. The carbonyl C–O is 1.15 Å while the two C–O lengths in the ring are 1.33 Å and 1.40 Å. The C–C length is 1.52 Å. The carbonyl bond distance is, of course, less than the accepted value for a pure double bond, but the others seem not particularly unusual.

Two closely related molecules which have been reported independently are isonicotinic acid hydrazide, by Jensen (101) and nicotinamide, by Wright & King (102). The dimensions inside the pyridine ring agree well in the two reports, the four C–C bonds averaging 1.39 Å in one and 1.40 Å in the other while the two C–N bonds average 1.335 Å and 1.36 Å. C–C to the side chain is 1.48 Å in the hydrazide and 1.52 Å in the amide. The two values for C–O and C–N are almost identical, averaging 1.225 Å for C–O and 1.335 Å for C–N. The hydrazide N–N is 1.41 Å.

Brown & Corbridge (103) have completed their three-dimensional refinement of acetanilide. The plane of the aniline group and the plane of the acetamide group are inclined at an angle of about 38°. This inclination is accomplished chiefly by rotation about the bond from nitrogen to the carbonyl carbon and is caused by steric repulsion between the carbonyl oxygen and the benzene ring; another "overcrowded" molecule. Since rotation of this kind does not occur to any marked extent in simple peptides and since such rotation and steric repulsion must influence the vibrations of the amide group, it hardly seems a fair substance for use in testing polarized infra-red

absorption by the various bonds involved for use in interpreting polarized infrared studies of polypeptides and proteins.

Merritt continues his investigation of complexes which are of importance in analytical chemistry. With Cady & Mundy he has reported the structure of zinc 8-hydroxyquinolinate dihydrate (104). The zinc atom is at a center of symmetry and with the organic molecules chelated to it forms an essentially planar molecule with four planar bonds to zinc. At somewhat greater distances the waters are attached to zinc in such a way as to complete a distorted octahedron about the metal. The distances to zinc are, from H_2O, 2.27 Å; from N, 2.06 Å; and from O, 2.05 Å. These bonds subtend angles ranging from 80° to 87° at the metal. The bonds between light atoms in the benzene and pyridine rings cannot be measured with high accuracy because of the high scattering power of the zinc, but they agree with predicted values within their possible error.

Brandt & Livingston (105) have reinvestigated hexafluorethane while Swick, Karle & Karle (106) have reinvestigated hexachlorethane. Both investigations include the effects of hindered rotation in their interpretation. In C_2F_6, C–C is given as 1.51 ± 0.06 Å, intermediate between the divergent values previously reported for this substance, and C–F is 1.33 ± 0.015 Å. This latter is in excellent agreement with other recent values for this bond, including the result quoted above (55, 56, 57) for trifluormethyl derivatives. In C_2Cl_6, the values reported are: C–C, 1.57 Å, with an uncertain error of about ± 0.06 Å and C–Cl, 1.74 ± 0.02 Å. The potential barrier hindering rotation is extimated at about 4 kcal./mole for the hexafluoride. In the hexachloride the effects of torsional motions are combined with those due to general vibrations in such a way as to make separate estimates of either difficult. The minimum possible potential barrier is given as 7 ± 1 kcal./mole.

In the introductory paragraph it was stated that no mention would be made of researches which do not establish a structure in some detail. Exception to this rule must be made in favor of a series of papers from the Cavendish Laboratory under the general title "The Structure of Haemoglobin." For, although a detailed structure for haemoglobin is probably not to be expected in the immediate future, very notable advances were made public during 1954 (107, 108, 109). As outlined in earlier papers, there are a number of discrete hydration stages for haemoglobin and if one assumes that the shape of the protein molecule remains unaltered and that only the quantity of intermolecular water changes, a study of the way the diffraction intensities change with hydration leads to some knowledge of the shape of the molecule. This process is rendered more secure by considering also the intensity changes which ensue when salt is added to the intermolecular water. Perutz (107) has described this process in detail and has produced a set of signs for the larger spacings ($d \geq 6.5$ Å) of the ($h0l$) zone. It has also been discovered that crystals in which two of the free sulphydryl groups of the protein have been combined with either *para*-mercuribenzoate or with silver ion are iso-

morphous with crystals of the free protein, but exhibit significant changes in scattered intensities. It has been possible to locate the Hg atoms in the complex with mercury and to establish signs by the usual isomorphous replacement method. Green, Ingram & Perutz (108) found that this procedure checked the previously established signs in detail. The resulting Fourier projections of the different dehydration stages [Bragg & Perutz (109)], although undoubtedly correct, do not have sufficient resolving power to show any recognizable detail in the molecule. But there is thought to be no reason why the sign-determining process cannot be extended to higher orders of this zone and the resolving limit reduced to 2.5 Å or better. Unfortunately, the zone corresponds to a projection through 63 Å of structure and it is not at all certain that even this higher resolution will reveal significant details of molecular architecture. But we do have in these Fourier projections the first direct physical pictures of protein molecules at resolutions superior to those afforded by the electron microscope.

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KINETICS OF REACTIONS IN SOLUTION[1]

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In preparing this material, the reviewer has made no special effort to achieve either completeness or impartiality. The emphasis has been determined largely by his interests and prejudices; and the completeness of coverage, by the accessibility of the literature. In particular, the reviewer had depended entirely upon *Chemical Abstracts* for the listing and translation of Slavic and Japanese language articles. As a result, the coverage of this part of the literature is regrettably incomplete.

In scanning the international literature dealing with the kinetics of solution reactions, it becomes evident that the great majority of authors working in this field now express concentrations in terms of molarity. Also, the slovenly habit of reporting the rate constants of first-order reactions in terms of common rather than natural logarithms has now gone out of fashion. However, there is no unanimity in the choice of units of time; minutes and even hours are used almost as often as seconds. In this day, when the use of the exponential notation for large and small numbers is universal, there appears to be no advantage in reporting rate data in units other than seconds.

Theory

While there have been no major developments in the general theory of the rates of reactions in solution, several important theoretical treatments of special cases have been published. Of particular interest is Noyes' (1) treatment of diffusion-controlled reactions. Christiansen (2) has examined the approach to the steady state in nucleation processes and concludes that commonly the steady state is attained so rapidly that the use of the ordinary approximation is justified. Cvetanovic & Whittle (3) have considered the errors which may be introduced into the calculation of the rate constants of the reaction steps when the steady-state approximation is applied to data obtained under conditions of intermittent illumination, etc.

There have been a number of attempts to predict the mechanisms of reactions (4, 5) and points of special reactivity of molecules (7 to 11) from structural considerations. These calculations have usually been made by the LCAO modification of the molecular orbital method. Coulson (9) has developed a simplified method for the calculation of points of reactivity in conjugated, especially aromatic, molecules. Jaffé (12, 13) has applied the molecular orbital method to the prediction and interpretation of the constants of Hammett's equation.

McBride & Villars (14) have presented a clear outline of the application of statistics to reaction-kinetic data, especially emphasising the often neg-

[1] The survey of literature pertaining to this review was concluded in November, 1954.

lected, proper weighting of data in least-squares calculations. Two papers (15, 16) dealing with the solution of the simultaneous differential equations which arise from the mechanisms of (relatively simple) complex reactions have been published. Melander (17) has discussed calculation methods for exchange reactions whose kinetics are unknown.

Isotopic Effect

One of the most powerful tools for the investigation of the details of kinetics is the determination of the effect of isotopic substitution on the rate of chemical reactions (18). By the use of deuterium-substituted piperidine in a study of its reaction with *p*-nitrochlorobenzene, Hawthorne (19) has ruled out the possible occurrence of a hydrogen-bonded configuration of the transition complex. Bryce-Smith *et al.* (20), who studied the metalation of benzene and toluene with potassium, report rate constant ratios, $k(H)/k(D)$, of 2.0 and 4.5 for the benzene reaction at 75 C. and the toluene reaction at 20 C., respectively. Wiberg (21) has examined the effect of deuterium substitution in benzaldehyde upon its rate of oxidation by $CrO_4^=$, its Cannizzaro reaction, and its benzoin condensation. The ratio, $k(H)/k(D)$, for the chromate oxidation was 4.3, which is within the predicted range. The ratio for the Cannizzaro reaction was somewhat smaller, being 1.8. The results for the benzoin condensation are somewhat ambiguous, but apparently are not consistent with the usually accepted mechanism of this reaction. Kaplan (22) reports that tritium-substituted ethanol is oxidized by Br_2 0.15-fold less rapidly than is normal ethanol.

Yankwich & Belford (23) in a study of the carbon-isotopic effect on the decarboxylation of malonic acid, dissolved in quinoline, have observed a difference in rate somewhat greater than was predicted, and ascribe this difference to a solvation equilibrium preceding the reaction. Working with molten malonic acid, at about 140°C., Yankwich & Promislow (24) obtained a value of 1.029 for $k(12)/k(13)$. Combining this with an older and less accurate value, $1.06 \pm .02$, for $k(12)/k(14)$, they calculate that $k(13)/k(14)$ should be $1.03 \pm .02$. Yankwich, Promislow & Nystrom (25) have carefully repeated these measurements and report values of 1.0545, 1.0285, and 1.0191 for $k(12)/k(14)$, $k(12)/k(13)$, and $k(13)/k(14)$, respectively. Since the last of these values is in good agreement with Bigeleisen's prediction, they conclude that there is nothing anomalous about the C^{13} effect in the decarboxylation of malonic acid. As far as the C^{13} effect is concerned, this appears to eliminate the need for and the experimental support of Pitzer's (26) ingenious suggestion that the reaction is "catalyzed" by the nuclear magnetic moment of C^{13}. Accordingly, the reported (26) catalytic effect of Dy^{+++} on this reaction is in need of re-examination. In the condensation of benzoyl benzoic acid to anthraquinone, Stevens & Crowder (27) have reported a reverse isotopic effect, $k(14)/k(12) = 1.07$. They attribute this unusual observation to the fact that a C—C bond is being formed rather than broken in the transition state.

Bartholemew *et al.* (28, 29) have observed a chlorine isotope effect, $k(35)/k(37) = 1.008$, in the solvolysis of *t*-butylchloride.

Experimental Technic

Aside from important advances in the study of fast reactions there has been no outstanding progress in the experimental technic of rate measurements. It has been pointed out (30, 31, 32) that the measurement of the intensity of fluorescence of a reactant is a convenient way of following the progress of certain reactions. Schwabel & Berg (33) have presented a detailed outline of the application of polarography to the study of reactions of moderate velocity. Bévillard has published an extensive review of the use of isotopes in the investigation of the kinetics of inorganic (34) and of organic reactions (35). Larsen & Kraus (36) have outlined a precise conductimetric method for following the course of a reaction and have applied it to a study of the interaction of alkyl halides and tertiary amines.

Fast Reactions

Measurements of the rates of fast reactions have received, in recent years, increasing attention from students of kinetics. Discussion 17 of the Faraday Society should rank as a landmark of progress in this interesting field. The second half of this volume of *Discussions* deals with solution reactions, whose half-times range from 10^{2} to 10^{-9} sec.

Several new analytical methods for following the course of chemical reactions have been proposed. Kolthoff & Reynolds (37) have developed the technic for the analytical use of a rotating or stationary Pt electrode and have applied it to the study of reactions between aquoferrous ions and hydroperoxides. Elving (38) recommends the use of a megacycle frequency oscillator in conductance (or capacitance) measurements. Both of these methods should have resolving times much shorter than the shortest available times of mixing. An improved recording interferometer has been constructed by Burnett, Deas & Melville (39). While this apparatus should prove useful in the study of polymerization, it is doubtful that it would be convenient for studying ordinary chemical reactions. Bengough & Melville (40) have described a thermometric method of following the course of a moderately fast reaction ($\tau_{1/2} > 0.1$ sec.) which can be initiated photochemically.

Eight papers which were presented at the Faraday Discussions are concerned with improvements and modifications of the well-known straight-tube and capacity-flow methods for the study of fast reactions. Chance (41) and Chance & Legallais (42) described the detailed construction and fundamental theory of a regenerative (i.e., recycling) flow method, which is designed to conserve rare reagents, such as pure enzymes. Dalziel (43) has modified the constant flow method so that it can be used with a Beckman spectrophotometer. A photometric apparatus, in which the scanning beam automatically traverses the length of the flow tube and records, electronically, the intensity

of the transmitted light as a function of position along the tube, is described briefly by Caldin & Trowse (44). Photoelectric photometry has been applied to the stopped-flow technic by Gibson (45). A versatile flow calorimeter for the study of fast reactions has been constructed by Pearson, Pinsent & Roughton (46). Temperature is recorded with a single-junction thermocouple provided with an optical-electronic amplifier. For the study of reactions having half-times between 5×10^{-2} and 2 sec., Pinsent (47) has designed and tested a flow system with two successive mixing chambers; the second mixer serving to quench the reaction. The relative advantages and limitations of the capacity-flow method are outlined by Denbigh & Page (48).

The rates of very fast reactions ($\tau_{1/2} \sim 10^{-9}$ sec.), especially of acid-base reactions, can be determined by measuring the relaxation time of the system. In this method an environmental property, such as temperature or electric field, of a system in equilibrium is changed rapidly, and the lagging response of a chemical equilibrium is observed directly or indirectly. The implied changes may be either periodic or isolated impulses. Eigen has published two important papers (49, 50) dealing with these methods and their application to particular cases. The experimental methods which he considers are (*a*) the absorption of sound as a function of frequency, (*b*) the electrical impulse method, and (*c*) the measurement of conductance changes following a "temperature jump" produced by a high tension impulse. Pearson (51) has discussed a similar approach utilizing the measurement of the power loss from a radiofrequency field. The present, rather scant, results which have been obtained by these methods are generally in accord with expectations, although there are a few interesting deviations. It is perhaps worth recalling (52) that the rates of dissociation and recombination of weak acids in their electronically excited states can be readily estimated from their easily measurable intensities of fluorescence in solutions of differeng pH. The rates of very fast acid-base reactions have been estimated semi-quantitatively by Ogg (53) from measurements of high-resolution nuclear magnetic resonance spectra.

The application of constant-current voltametry to the study of the kinetics of fast reactions has been reviewed by Delahay (54), who also compares this technic to the corresponding polarographic method. The polarographic methods have also been developed and applied by Pliva & Smutek (55) and by Koryta and co-workers (56, 57, 58). These latter methods have the advantage that they are not limited to proton-exchange reactions, but the interpretation of the results have been difficult and in some cases uncertain. Wiesner, Wheatley & Los (59) have applied the polarographic method to the determination of the rates of recombination of phenylglyoxalate anions with various proton donors.

The quenching of the fluorescence of dissolved substances is a type of fast bimolecular reaction whose rate can be estimated, indirectly but simply, from measurements of light intensity. Svirbely & Sharpless (60) have demonstrated that the quenching of eosin by iodide ions varies with ionic strength,

dielectric constant, and viscosity, as expected. Harty & Rollefson (61) measured the quenching of the doubly-positive quinine ion by Br^- and of the doubly-negative fluorescein ion by I^-. They report that the effect of electrolytes upon the rate of quenching is consistent with the Debye-Hückel approximation, but that it exhibits marked specific-ion effects. Measurements of the quenching of the fluorescence of anthracene in liquid solutions have been reported and discussed by Melhuish & Metcalf (62). Noyes (1) has published a theoretical analysis of diffusion-controlled reactions and has applied this analysis to the case of fluorescence quenching.

Several years ago, Porter and Norrish demonstrated that it is practicable to determine the kinetics of the disappearance of radicals and other labile species, which can be produced photochemically by an intense flash of short duration. The half-lives of reactions, which can be measured by the flash photolytic method, are not limited by (relatively slow) mixing times, but only by the duration of the flash. Porter & Windsor (63) have applied this flash photolytic technic to the study of the disappearance of the lowest triplet state of anthracene, and related molecules, in fluid solutions at ordinary temperatures. These rates of decay are strictly first-order. For anthracene in hexane the half-life is about 6×10^{-5} sec. Surprisingly enough, the rate constant of this first-order process is inversely proportional to the square root of the viscosity of the solvent. Livingston, Porter & Windsor (64) have published a preliminary account of a similar study of the triplet states of chlorophyll and similar compounds. As has been pointed out by Sangster (65), a pulse of high-energy electrons can be used to produce a high concentration of OH and H in aqueous solutions and, therefore, it may be possible to follow their recombination by direct photometric measurements.

Bell and his co-workers (66) have improved the thermal-maximum method for measuring the rates of moderately rapid ($T_{1/2}>0.2$ sec.) reactions. The measurements are precise and simple, but this method is limited to reactions having simple kinetics, preferably first or second-order.

Pearson & Piette (67) have revised and modified the steady-state reaction method of following a moderately rapid reaction. In this procedure, the concentration of one reactant is maintained constant by the continuous, metered addition of a reagent to the stirred reactor. When first used by Brönsted and Kilpatrick in 1929, an indicator served to measure the pH and the reagent was added as a concentrated solution from a continuously-flowing microburet. The present authors measure the pH with a glass electrode and add OH^- electrolytically.

Acid-Base Catalysis

Although many reactions which involve acid-base catalysis have been investigated during the past year, the study of the subject per se has received relatively little attention. It is of interest that three of the papers on this general subject are devoted to reactions in "super acid" solutions (68, 69, 70) and three to catalysis by Lewis acids (71, 72, 73).

Papers have appeared discussing the catalytic effect of Brönsted acids and bases upon exchange reactions (74, 75), keto-enol isomerizations (71), condensation and addition reactions (76 to 81), hydrolyses of organic compounds (76, 82–88) and of phosphate ions (89, 90), elimination processes (91), and oxidation-reduction reactions (92). The base-catalyzed isotopic exchange between $CDCl_3$ and H_2O has been studied by Hine, Peek & Oakes (74), who report that the reaction is catalyzed by general bases as well as by OH^-. Weston & Bigeleisen (75) have made extensive measurements of the H—D exchange between PH_3 and H_2O. On the basis of their results and certain reasonable assumptions regarding the kinetics, they estimated that the basic and acidic dissociation constants of PH_3 are 10^{-28} and 10^{-29}, respectively. Evans & Young (5), by measuring the rates of bromination of various dialkyl ketones, have determined the rates of the acid-catalyzed keto-enol isomerizations of these compounds and have related these results to the structures of the molecules.

The basic-catalyzed condensations of aldehydes with ketones and with nitro paraffines have been studied, respectively, by Dubois & Luft (77) and by Boileau (79). Gibert (76) has proposed a detailed mechanism in explanation of Bell's published measurements of the acid- and base-catalyzed hydration of acetaldehyde. Lemaitre, Smets & Hart (80) have investigated the acid-catalyzed condensation of thiourea with formaldehyde. Some interesting results of a study of a cyanhydrin synthesis have been published by Prelog & Wilhelm (81). This reaction, which took place in a nonionizing solvent, required the simultaneous action of an acid and a base. When an asymmetric alkaloid served as the base, some preferential asymmetric synthesis was observed.

The basic hydrolysis of simple esters has been studied by Tommila & Hietala (82) and by Sauterey (86). De Roo & Bruylants (87), who measured the rates of the acid- and the base-catalyzed hydrolyses of amides of aliphatic acids, have observed that these rates are closely related to those of the corresponding ester hydrolyses. De Wolf & Roberts (85) have studied the acid catalysis of the hydrolysis of ethyl orthoformate in aqueous-dioxane solutions and have reported that general acid catalysis occurs. This is in marked contrast to the earlier measurements of this reaction in aqueous solutions where only specific hydronium ion catalysis was detectable. Barnum & Gorin (93) have re-examined Dawson's (1953) data on the acid hydrolysis of ethyl acetate and have come to the conclusion that there is no evidence supporting the view that HSO_4^- is an efficient catalyst.

Extensive and accurate measurements of the acid-catalyzed hydrolysis of the pyrophosphate ion have been made by Campbell & Kilpatrick (90), who, by using P^{32} as a tracer in their analyses, were able to extend their measurements to dilute solutions of the reactant where the pH of the solution was practically constant during the progress of the reaction. Crowther & Westman (89) have shown that, while the hydrolysis of triphosphate to pyrophosphate is both base- and acid-catalyzed, the hydrolysis of pyrophosphate to orthophosphate is catalyzed by acids only.

Bell & Brown (68) have extended the study of the depolymerization of paraldehyde to concentrated aqueous solutions of strong acids. When HCl, $HClO_4$, H_2SO_4, or HNO_3 is used as the catalyst, the rate is proportional to the product of Hammett's acidity function and the concentration of the polymer. Somewhat more complex results were observed in solutions of weaker acids, as dichloracetic acid or $KHSO_4^-$. Foster (70) has interpreted his measurements of the acid-catalyzed phenol-styrene reaction occurring in acetic acid as indicating that the effective catalytic acid is $CH_3 \cdot COOH_2^+$.

Braude & Gore (71) have investigated, in an aprotic medium, the BF_3 catalysis of the rearrangement of phenyl ally alcohol to cinnamyl alcohol. Since water retards the reaction, the catalysis is not attributable to HF but to BF_3 itself, which probably complexes with the hydroxyl group. It has been demonstrated by Coleman, Newman & Garrett (72) that the decomposition of benzazide, in aprotic solvents, is catalyzed by such Lewis acids, as $GaCl_3$, $AlBr_3$, $FeCl_3$, $TiCl_4$, etc. The authors estimated the relative acidities of these reagents from their observed catalytic efficiencies.

Electron Transfer Reactions

Recent experimental and theoretical studies (94 to 98) have contributed greatly to our understanding of electron transfer reactions, which were formerly the subject of a controversy more spirited than sensible. At present, the following facts appear to have been established. The transfer of either one or two electrons (or the corresponding exchange of atoms) can occur during a single collision; that is, while the transition complex persists. The proof that chemical reactions in solution can occur by means of electron transfer unaccompanied by the transfer of nuclei is none too definite, but it is difficult to interpret some experimental results [e.g., the study (99) of the reaction $IrCl_6^{=} + Cr^{++} = IrCl_6^{\equiv} + Cr^{+++}$] in any other way. Although atom and electron transfer reactions are frequently kinetically indistinguishable, they are not essentially similar but, in some important respects, are distinctly different processes (95). The theoretical treatment of exact-resonance electron transfer between atoms in dilute gases is not applicable, even in a reasonably modified form, to electron transfer reactions in solution (95). Since energy would be required to rearrange the water molecules which make up the hydration shells of the ions, the probability of close approach (corresponding to interpenetration of these shells) of the ions is greatly reduced (94 to 98, 100). Marcus, Zwolinski & Eyring (100) have made a painstaking quantitative analysis of the electrostatic interactions of a system composed of two ions, such as Fe (II) and Fe (III). They conclude that electron tunneling is responsible for most electron transfer reactions and that "the best distance for electron transfer is usually at a sufficiently large distance that the two reacting ions interfere negligibly with each other's hydration shells." A careful, although qualitative, consideration of this same problem led Platzman & Franck (95) to decide that any analysis of the electron transfer problem in terms of purely coulombic interactions would be profitless. They further conclude that, when two ions [e.g., Fe (II) and Fe (III)] are so widely

separated that their hydration configurations do not interpenetrate, electron transfer is impossible. Ions, such as halide or hydroxyl, can serve, in the transition complex, as a bridge for the transfer of an electron between two positive ions (97, 99, 101). This bridge effect occurs in addition to, and is more important than the reduction of the coulombic repulsion between the ions of like charge (97, 99, 101).

Information regarding electron transfer processes has been obtained by studying oxidation-reduction reactions as well as exchange and substitution reactions of ions and simple molecules. Taube and his co-workers have successfully measured (99, 101) simultaneously oxidation-reduction reactions and the concurrent exchange of complexing groups. The hydrated Cr^{++} is oxidized much more rapidly by $[Co(NH_3)_5Cl]^{++}$ than by $Co(NH_3)_6^{+++}$ or $Co(H_2O)_6^{+++}$. The Cl^- is transferred quantitatively to the resulting Cr ion. Under the experimental conditions, exchange with free Cl^- in the solution was negligible. It follows that Cl^- forms a bond, in the transition complex, between the Co and Cr ions. While these results could be interpreted as a Cl atom transfer process, comparison with other reactions (e.g., the oxidation of Cr^{++} by $IrCl_6^=$) makes it appear more probable that an electron is transferred across the halide bridge, after which the halide ion remains attached to that positive ion with which it forms the more stable complex. This interpretation has been substantiated by measurements (101) of the (rapid) exchange of Cr^{61} between Cr^{++} and $CrCl^{++}$.

Anderson & Bonner (102) and van der Straaten & Aten (103) have studied an isotopic exchange between hydrated Cr^{++} and Cr^{+++}. The exchange goes by two parallel paths, one by way of the simple hydrates and the other, a faster reaction, involves a complex in which one water is replaced by an hydroxyl ion. These reactions probably involve a hydrogen atom transfer. No catalysis of the reaction was observed when a chloride was added to the solution. This inactivity of the Cl^- appears to be a consequence of the stability of the hexahydrated Cr^{+++}. Wolfgang & Dodson (104) have measured an isotopic exchange between Hg^{++} and $HgCN^+$, and have demonstrated that the rate of ionization of $HgCN^+$ is less than 6×10^{-1} sec^{-1} $[HgCN^+]$. It appears plausible that the transition complex for the exchange reaction involves a CN^- bridge.

George & Irvine (105) list twelve oxidation-reduction reactions, between ions, which occur "instantaneously on mixing." The oxidizing agents were hydrated or complexed ions of Ir(IV), Fe(III), Ru(III), or Ce(IV) and the reducing agents were complexed Fe(II), Ru(II), or Mo(II) ions. The complexing agents were Cl^-, CN^-, dipyridil, or pheanthroline. Nine of the twelve reactions are fast in spite of the fact (97) that they occur between ions having charges of the same sign.

Oxidation-Reduction Reactions

The kinetics of an interesting reaction, the reduction of cupric acetate by H_2 in aqueous solution, were studied by Halpern & Dakers (106, 107). The

reaction is first order in respect to each of the reactants and is moderately rapid, having a second-order rate constant of $8\times10^{11}\exp(-24{,}200/RT)\ m^{-1}$ sec.$^{-1}$. When only the two reagents are present, Cu_2O is precipitated; but, in the presence of dichromate, cupric acetate acts as a catalyst for the reduction of $Cr_2O_7^{=}$ to Cr^{+++}.

The study of the reduction of H_2O_2 (108 to 111) and of organic hydroperoxides (112) have been continued. Weiss and co-workers (109) report that, by a proper choice of concentrations and the use of pure materials, it is possible to measure the reduction of H_2O_2 by Fe(II) without concurrent decomposition of H_2O_2. They found the rate of the reaction to be equal to $k[H_2O_2][Fe^{++}]$, where $k=1.05\times10^{-3}\exp(-8460/RT)\ m^{-1}$ sec.$^{-1}$.

There have been two new investigations (113, 114) of the decomposition of O_3 in aqueous solution. Forchheimer & Taube (114) have demonstrated that isotopic exchange between O_3 and H_2O occurs only when O_3 is decomposing. They conclude from the observed limiting value for the induced exchange that OH certainly acts as an intermediate in the O_3 decomposition.

Eager & McCallum (115) were unable to detect isotopic exchange between $S_2O_8^{=}$ and $S^*O_4^{=}$ after 12 hr. at 34°C. in either water or acetic acid, thus eliminating the equilibrium ($S_2O_8^{=}=SO_4^{=}+SO_4$) as a possible step in $S_2O_8^{=}$ reductions.

Studies of diazotization (92), the reduction of HNO_2 by HCOOH (116), the reaction between HNO_2 or amyl nitrite with amines (117), the reaction between HNO_2 and H_2O_2 (108), and the exchange of O^{18} between HNO_2 and H_2O (108) have all been measured. All of these reactions have been interpreted in terms of the intermediate $H_2NO_2^+$ or its anhydride, NO^+.

The reduction of ClO_4^- with V(II) and V(III) has been studied by King & Garner (118) and with Ti(III) by Duke & Quinney (119). The vanadium oxidations appear to be kinetically simple, but the latter authors report that the kinetics of the oxidation of Ti(III) are complex and involve several alternative paths.

De la Mare, Ketley & Vernon (120) have investigated the reduction of HClO by anisole under conditions in which the reactions of ClO^- and Cl_2 could be neglected. The authors postulate that the rate-determining step is the formation of the intermediate, Cl^+. This mechanism is formally analogous to the well-established mechanism for the nitration of aryl hydrocarbons which involves NO_2^+. However, there does not appear to be any confirmatory evidence for the Cl^+ mechanism. From an analysis of the effect of common ions and of electrolytes upon the rate of halogenations occurring in acetic acid solutions, Robertson (121) concludes that molecular halogens react directly, not by way of either X^+ or any solvated form of this unstable ion. Ellis & Soper (122) have postulated that Me_3NCl^+ is the chlorinating agent in aqueous solutions of amines.

The study of the kinetics of the oxidation of glycol and methyl-substituted glycols by IO_4^- has been continued by Duke & Bulgrin (123) and by Buist & Bunton (124). Although the new results confirm the earlier findings and

conclusions, the kinetic role of the IO_4^--glycol complex remains in doubt. Malaprade & Coulombeau (125) report that, in dilute solutions of low acidity where the direct reaction of IO_4^- and oxalic acid is very slow, this reaction is induced by the reduction of Ag(III) or Cu(III). Morgan (126) has published a critical review of the kinetics of reactions of iodine and its oxidative ions.

Branch & Jones (127) have investigated the oxidation of aromatic ethers by HBrO, and they postulate that the mechanism involves the ion H_2BrO^+. Tsuruta *et al.* (128) have shown that I_2 catalyzes the reaction between Br_2 and toluene. They interpret their results in terms of the intermediate, IBr. The rate of decomposition of BrO^- has been investigated (129) in aqueous solution.

It has been shown (146) that the rate of the reaction between Np(IV) and the Np(VI) obeys the simple kinetic law,

$$-d(\mathrm{Np(IV)}/dt = k[\mathrm{Np(IV)}][\mathrm{NpO_2^{++}}][\mathrm{H^+}]^2.$$

Two plausible mechanisms have been suggested, one of which involves the transfer of a hydrogen atom, the other, an oxygen atom. Symons (130) has demonstrated, by the use of a tracer technic, that when MnO_4^- decomposes in a basic solution, $2OH^- + 2MnO_4^- = 2MnO_4^= + H_2O + 1/2\ O_2$, the oxygen is derived entirely from the water. Unlike MnO_4^-, $MnO_4^=$ exchanges O rapidly with the solvent. Drummond & Waters (131) have studied the oxidation of malonic acid by manganic pyrophosphate, and they conclude that radicals are intermediate in the reactions. Hinshelwood and co-workers (132) have studied the oxidation of $TiCl_3$ by azobenzene, etc. and have suggested a mechanism which is consistent with their data. The study of the reactions involving Fe(II), Fe(III), quinones, and hydroquinones has been extended by Baxendale & Hardy (133) to conclude several substituted quinones. The kinetics are similar to those observed previously for benzoquinone.

Two reviews (134, 135) of the autoxidations of certain classes of organic compounds have been published. Banks *et al.* (136) have considered the role of heavy metal ions in autoxidations of organic compounds. Abel (137 to 141) has re-examined the mechanisms of certain classical autoxidation reactions. Briner & de Chartanay (142) have applied infrared analysis to the study of the autoxidation of benzaldehyde. Letort and co-workers (143, 144, 145) have investigated the autoxydation of dibenzyl ether and have shown that this reaction has a chain mechanism.

Exchange and Substitution Reactions (Inorganic)

The study of isotopic exchange reactions of complex ions in aqueous solution has contributed greatly to our understanding of both the kinetics and the equilibria of such ions. Amphlett (98) has published an excellent comprehensive review of this subject. Current investigations indicate that many supposedly simple reactions, of this type, actually proceed by surprisingly complicated reaction paths. Of five systems which were carefully

investigated during the past year, only one, the uncatalyzed exchange of Cl^- between $AuCl_4^-$ and the simple Cl^-, can, by any stretch of imagination, be classed as a simple substitution reaction.

Rich & Taube (147) have demonstrated that the rate of this reaction follows the following equation:

$$-\frac{d[Cl^-]}{dt}\,(m \text{ sec.}^{-1}) = 20 \exp\left(\frac{-4,500}{RT}\right)[AuCl_4^-] + 3 \times 10^{12} \exp\left(\frac{-16,500}{RT}\right)[AuCl_4^-][Cl^-]$$

The authors postulate that the first term of this expression corresponds to the rate-controlling step, $H_2O + AuCl_4^- \rightarrow [AuCl_3(OH)]^- + Cl^- + H^+$, followed by a rapid substitution of Cl^- for OH^-. Ferrous ion catalyzes (i.e., induces) this reaction, and the same authors (148) have interpreted the results of their well-planned experiments as follows: The ferrous ion, being a single-electron reducing agent, reacts to form Au(II). The chloride complex of this ion is labile and exchanges Cl^- rapidly with the solution. It can also undergo an efficient electron transfer reaction with $AuCl_4^-$. Rich & Taube (149) have also shown that the exchange of Cl^- between $PtCl_4^=$ and $PtCl_6^=$ is a chain reaction induced by the active species, $PtCl_5^=$. This ion is formed photochemically, and the reaction is sensitive to the presence of inhibitors. The exchange of Np^{239} between Np(IV) and Np(VI), which was studied by Sullivan, Cohen & Hindman (150), is likewise complex and appears to involve a dismutation equilibrium. Fava & Pajaro (151), who have studied the exchange of S between $S_2O_3^=$ and $S_3O_6^=$, conclude that the reaction is a result of the dissociation equilibrium, $S_3O_6^= = S_2O_3^= + SO_3$. Hunt & Plane (152) have measured the rate of exchange of H_2O between $Cr(H_2O)_6^{+++}$ and the solvent. The process is relatively slow, having a value of 3×10^{-6} sec.$^{-1}$ for k at 27°C. and one of 28° kcals for the energy of activation. Van der Straaten & Aten (153) have shown that the exchange between Cl^- and the green chromic chloride complex ion is a slow process.

The formation of mononitrito- and mononitro-cobalt-ammines from NO_2^- and $[Co(H_2O)(NH_3)_5]^{+++}$ has been investigated by Pearson *et al.* (154). Like the isotope exchange reactions, this apparently simple substitution process has a very complicated mechanism. Poulsen, Bjerrum & Poulsen (155) have measured the rate of uptake of SCN^- by $Cr(H_2O)_6^{+++}$. The frequency factor, pZ, for this reaction is not much greater than 10^{11} m^{-1} sec.$^{-1}$, in spite of the fact that it involves two ions of unlike sign. Taken in conjunction with the very rapid rates which George & Irvine (105) observed for reactions between two ions of the same sign, this suggests that the theoretical treatment of the frequency of collisions between ions has exaggerated the effect of coulombic forces.

Exchange and Substitution Reactions (Organic)

Judging from the number of papers, the kinetic study of organic substitutions is more popular than that of any other class of reactions. Whether one

regards the Ingold system of classification of these reactions merely as a convenient bookkeeping scheme or believes that its introduction constituted a fundamental advance in our understanding of the subject, one must admit that its use has greatly stimulated the study of these reactions. It has brought, at least apparent, order into a field which was once chaotic. On the dark side of the ledger should be placed the fact that the SN_1—SN_2 scheme is certainly an over-simplification. It is regretable that some of the physical-organic chemists who work in this field appear to regard this scheme as infallible doctrine and to use SN_1 and SN_2 as Procustean beds into which all substitution reactions are to be fitted regardless of how much violence must be done to the kinetic observations.

Prévost (156) has discussed Ingold's classification from the viewpoint of systematic terminology. A slight modification and addition to the scheme has been suggested by Anbar *et al.* (157). Winstein (158) has again emphasized the importance of distinguishing between "internal ion pairs," "solvent-separated ion pairs," and dissociated ions, in the consideration of the ionic mechanism of substitution reactions. Ingold (159) has postulated that there exists a whole series of substitution mechanisms, which are hybrids of and intermediate between SN_1 and SN_2. He states,

> We can give these two situations a common description by assuming that, around any alkyl halide molecule, a certain volume v, which would be small in the bimolecular case but large in the unimolecular, can be described, such that, when no reagent particle is inside of it, the probability of decomposition of the alkyl halide molecule is small at best, whereas when at least one reagent particle is within, the probability of reaction is large and characteristic. By now allowing v to vary without restriction from one reaction to another, we can conceptually connect the two limiting molecular mechanisms with a continuous chain of intermediate mechanisms.

The reviewer is of the opinion that this concept is not useful, and ventures to predict that it will not find support, either from dependable experimental results or from sound and definite theoretical analysis.

A general, rather brief review of isotopic exchange reactions has been published by Herber (160) and a review of the several types of slow and fast H—D exchanges by Brodskii (161). The rapid H—D exchange between amines and alcohols has been studied by Hine & Thomas (162) and between methanol and water by Kwart, Kuhn & Bannister (163). Swain, *et al.* (164) have investigated the H—D exchange between NH_4^+ and methanol in a dimethyl formamide solution. The rate of the base-catalyzed exchange between $CDCl_3$ and H_2O has been measured by Hine, Peek & Oakes (74). Olsson & Melander (69) have determined the relative rates of *o*-, *m*-, and *p*-tritium-substituted toluene exchange with an 81 per cent H_2SO_4 solution. The isotopic exchange between elementary S and organic sulfides has been investigated by Gur'yanova (165). The same author (166) has studied the S^{35} exchange between polysulfides, and concludes that this reaction involves the formation of RS radicals. The rate of exchange between I^- and nitro-

benzyl iodide has been measured by Purlee, Kahn & Riebsomer (167), and between I^- and iodoacetic acid, etc. by van der Straaten & Aten (168). The heat of activation of each of these reactions is approximately 16 kcals.

The number of papers dealing with substitution reactions is so great that it is not practicable to consider them individually in this review. The aim of the majority of these studies was to find a relation between the reactivity of a molecule and the nature of its substituent groups. In a number of cases an attempt was made to explain these results in terms of qualitative or semi-quantitative theories of structure. The solvents used vary all the way from hexane, through liquid SO_2, to water. Usually values are reported for the Arrhenius factors, pZ and E, but frequently too few measurements were made of a single reaction to permit the rate law to be definitely established. The greatest number of these papers deal with hydrolytic (82 to 87, 157, 169 to 186) and solvolytic reactions (171, 177, 181, 187). Others are concerned with the Mentshutkin reaction (19, 36, 83, 159, 188 to 193), or with the substitution of a halide ion by another halide or $S_2O_3^=$, etc. (6, 163, 194 to 205.)

Elimination and Decomposition Reactions

The kinetics of a number of elimination reactions, especially decarboxylations, have been investigated during the past year. The intramolecular C^{13} and C^{14} isotope effects on the decarboxylation of malonic acid have been measured carefully (23, 24, 25), and it appears that, contrary to last year's view, these effects are not anomalous. The acid-catalyzed decarboxylation of *p*-amino salicylic acid has been studied by Willi & Stocker (206), and of uronic acid, etc. by Meller (207). Pettersen (208) has investigated the decarboxylation of oxaloacetic acid, which is catalyzed by analinium ion, etc.

Davies, Davies & Stoll (209) have observed that the elimination of Br^- (presumably by simple ionization) from ω-bromo undecanoic acid, etc., is followed by concurrent cyclization and polyester formation. Cristol, *et al.* (210) have proven that the elimination of HBr from *cis* *p*-nitro β-bromostyrene is 2000-fold faster than the reaction of the corresponding *trans*-compound. Hill, *et al.* (205) have used D as a tracer in the study of the mechanism of β-elimination of HBr from alkyl bromides and have concluded that the reaction is a bimolecular process in which H^+ and Br^+ are removed simultaneously.

Szwarc and co-workers (211, 212) have investigated the effect of solvent and temperature upon the rate of decomposition of diacetyl peroxide and have also determined the products which are formed in benzene and in aliphatic-hydrocarbon solvents. Breitenbach and Kastel (213) have employed the peroxide-induced polymerization of styrol as an analytical method for following the rate of decomposition of anthracene peroxide in benzene solutions.

The kinetics of the homogeneous, alkaline decomposition of cyclotrimethylene-trinitramine were carefully investigated by Jones (214). Over-

berger, *et al.* (215) have studied the effect of steric factors on the decomposition of azo compounds, and Cohen (216), the role of solvent in the decomposition of a similar compound.

Addition and Condensation Reactions

The study of the kinetics of the addition of HClO to crotonic acid has been continued (217) and the analogous reaction with tiglic acid has been investigated (218) by Craw. The complicated rate equation, which is based upon extensive and apparently careful measurements, demonstrates that the reaction is far from simple and that it follows several parallel reaction paths. De la Mare & Pritchard (220) have investigated, in aqueous solutions containing $HClO_4$ and $AgClO_4$, the addition of HClO to $CH_2{:}CH{\cdot}CH_2Cl$ and the subsequent rearrangements of the product. Schwabe and Voigt (219) reported that the rate of the Hg^{++} catalyzed hydration of C_2H_2 in H_2SO_4 solution is first-order in respect to C_2H_2 and second-order in respect to H_3O^+.

The addition of aldehydes to a variety of compounds has been studied kinetically. These include a cyanhydrin synthesis (81), the addition of aldehydes to nitroparaffines (79), the reaction of *p*-nitrobenzaldehyde with *p*-dimethylaminoaniline (221), and the condensation of formaldehyde with thiourea (80). All of these reactions are acid- or acid-base catalyzed, and appear to obey relatively simple kinetic laws.

Petty & Nichols (222) have measured carefully the addition of HNO_3 to the ethylene oxide ring. Hansson (223) who has studied the addition of tertiary amines to propylenoxide, reports that the reaction, which is neither acid- nor base-catalyzed, has a specific reaction rate, k, which is related to the equilibrium constant K_B, of the base as follows—$k = 4.8 \times 10^{-9}\, K_B^{-1.8}$.

Isomerization Reactions

It has been demonstrated by Davies & Dwyer (224) that the role of racemization of tris (2:2′ dipyridyl) and tris (1:10 phenanthroline) ferric ions is greater than the rates of dissociation of these complexes. Basolo, Hayes & Neumann (225) made a similar observation for the corresponding complex ferrous ions. It follows that these racemization reactions are intramolecular processes. Davies & Dwyer (226) have also observed that the rates of racemization of the (+) and (−) forms of tris (2:2′ dipyridyl) nickel ions, in the presence of other optically active electrolytes, differ from one another. The authors attempt to explain this result in terms of the formation of addition complexes between the several ions.

The racemization, isomerization, and H—D exchange of alkanes in the presence of 96 per cent H_2SO_4 (227) or of halosulfonic acids (228) has been examined by Burwell *et al.* They interpret their results in terms of a chain mechanism in which a carbanion is the active species. Bokadia & Deshapande (229) have made a few measurements of the rate of the keto-enol isomerization of certain ketones in aqueous solution.

Photochemical Reactions

Photochemical measurements, in addition to their intrinsic interest, can provide valuable information about labile intermediates and their possible roles in thermal reaction. For example, the occurrence of diradicals as intermediates has often been postulated, but it has proven difficult to confirm their existence. Russell & Tobolsky (230) have produced a diradical by the photochemical splitting of the S—S linkage in 1,4,5 oxodithiacycloheptane, and have studied polymerization reactions initiated by it. The diradicals disappear rapidly by reforming the ring.

Definite experimental evidence for the existence of the cage effect has been obtained by Lampe & Noyes (231), who measured the quantum yield of the photochemical dissociation of I_2, in several solvents over a wide range of viscosities.

The *cis-trans* isomerization of substituted azobenzenes has been carefully investigated by Birnbaum & Style (232). Baril (233) has demonstrated that the quantum yield of the decomposition of *p*-diazo N—N dimethylaniline zinc chloride dihydrate in aqueous solutions is about one. Back and Sivertz (234) have shown that 2,2′ azobisisobutyronitrile is decomposed photochemically into radicals with a quantum yield of about 0.43.

Freed & Sancier (235) have shown that, even at 77°K. in a fluid solvent (composed of propanol, propane, and propene), UCl_4 can be photochemically reduced to UCl_3. It has been demonstrated by Heidt (236) that illumination of an aqueous solution containing UO_2^{++} and methanol produces U(V) ions. These ions disproportionate forming U(IV) and UO_2^{++}. The steady state of this system was studied intensively. Heidt & McMillan (237) have continued the study of Ce(III)-Ce(IV) solutions, and report that the quantum yield of the reduction of water by Ce(III) is about 0.0014. Emschwiller & Legros (238) have studied the photochemical hydrolysis of $Fe(CN)_6^{4-}$ to $Fe(H_2O)(CN)_5^{3-}$. In the absence of the reaction products, the quantum yield is about 0.44, but on continued illumination the thermal back reaction results in the establishment of a photochemical steady state.

As a consequence of further measurements of the photolysis of potassium ferrioxalate solutions in the presence of oxygen, Parker (239) has concluded that the effect of O_2 can be explained as resulting from a thermal oxidation of Fe(II) which induces the autoxidation of oxalate.

Several studies of dye-sensitized reactions have been reported. Melville & Richards (240) have completed a careful study of the photochemical autoxidation of isopropylbenzene using azonitrile as a sensitizer. The reaction is a radical chain process. Bolland & Cooper (241) have interpreted their measurements, of the photochemical autoxidation of ethanol sensitized by anthraquinone disodium sulfonate, as indicating that the reaction is a non-chain process, in which the primary act is the formation of a pair of radicals, one being a semiquinone. Oster (242) has reported that photo-induced dye-sensitized polymerizations are greatly accelerated by the presence of oxygen

and a reducing agent, presumably attributable to the formation of reactive radicals. Pestemer (243) has studied the photochemical reduction of thionine by allylthiourea, etc. His results are explicable in terms of the reaction of a long-lived excited dye molecule. Desai & Vaidya (244) have made some observations on the irreversible, photochemical bleaching of certain dyes.

Gemant (245) has studied oxidative ions which are formed when solutions of peroxides and aromatic diols, dissolved in hydrocarbons, are irradiated with ultraviolet light.

Derbyshire & Steacie (246) have investigated the photolysis of mercury dimethyl in hexane at temperatures ranging from 25° to −80°C. They interpret their results in terms of a "hot radical" mechanism.

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KINETICS OF REACTIONS IN GASES[1,2]

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Introduction

The reviewers have endeavored to consider selected topics in a critical fashion. We readily admit that our classification of papers into general topics is, to some extent, arbitrary. We further apologize for omission of some papers, including several interesting theoretical ones, because of limitations of space and of our competence.

Energy Transfer Processes

The transfer of energy on collision is a phenomenon of general importance in chemical kinetics. The excitation of vibrational energy on collision has been investigated principally by the study of the pressure dependence of unimolecular reactions, and by sound absorption and dispersion measurements. Experiments on fluorescence quenching and on photosensitization provide information about the conversion of electronic energy into other modes.

As is now well known, the rate-determining step in the N_2O_5, NO reaction is the unimolecular dissociation of N_2O_5, $N_2O_5+M \rightleftharpoons N_2O_5^*+M$, (reactions 1, 2), $N_2O_5^* \rightarrow NO_2+NO_3$ (reaction 3); at the low pressure, second-order limit, the rate-determining reaction is reaction 1. Wilson & Johnston (1) have extended the studies of the latter author to include the effects of various noble gases and of CCl_4 as M and have tabulated the relative efficiencies of these, along with other gases studied previously, for vibrational deactivation (reaction 2): He, 0.0650; Ne, 0.0855; A, 0.154; Kr, 0.208; Xe, 0.189; N_2, 0.228; NO, 0.300; CO_2, 0.387; CCl_4, 0.673; SF_6, 0.443; N_2O_5, 1.00.

The rate of the very fast reaction $N_2O_4 \rightarrow 2NO_2$ (reaction 4) has been measured in the presence of the inert gases N_2 and CO_2 by a photoelectricoscillographic method using a shock wave in a shock tube to rapidly heat the mixture and initiate reaction [Carrington & Davidson (2)]. At 1 atm., this unimolecular reaction is at its low pressure second-order limit and, for the step, $N_2O_4+M \rightarrow N_2O_4^*+M$, (reaction 5) $k_{5(N_2)}=k_{5(CO_2)}=2\times10^{17}$ exp $(-11{,}000/RT)$ cc. mole^{-1} sec.$^{-1}$. At several atmospheres, there are indications of the transition to first-order behavior and it is suggested that the first-order rate constant is 10^{16} exp $(-13{,}000/RT)$ sec.$^{-1}$. The large value of the frequency factor is expected for this kind of a dissociation process. Bauer & Gustavson (3) report an impact tube measurement of the rate of (reaction 4) at one temperature and pressure which indicates that an NO_2, N_2O_4 mix-

[1] The survey of the literature pertaining to this review was concluded in December, 1954.

[2] Contribution No. 1961 from the Gates and Crellin Laboratories.

ture is about seven times more effective for activating N_2O_4 than are N_2 and CO_2.

Cordes & Johnston (4) have studied the rate of thermal decomposition of nitryl chloride, which presumably proceeds according to the mechanism of Schumacher & Sprenger (5),

$$NO_2Cl \rightarrow NO_2 + Cl \qquad 6.$$
$$Cl + NO_2Cl \rightarrow NO_2 + Cl_2 \qquad 7.$$

The rate determining reaction, (reaction 6), is a unimolecular process and is, under the accessible experimental conditions, at the low pressure second-order limit. In pure NO_2Cl, $k_6 = 5.8\ (\pm 0.6) \times 10^{16} \exp\ (-27{,}500(\pm 100)/RT)$ cc. mole^{-1} sec.$^{-1}$; the number of vibrational modes contributing to the reaction is estimated from the Slater theory to be 6, the number of normal modes of the molecule. Argon is less efficient and NO_2 about as efficient in deactivation as NO_2Cl.

Our knowledge of the important reaction, $CH_3+CH_3 \rightarrow C_2H_6$ (reaction 8), has been further advanced; interest has focussed on the pressure dependence of reaction 8 and on its detailed mechanism,

$$CH_3 + CH_3 \rightleftharpoons C_2H_6^* \qquad 9, 10.$$
$$C_2H_6^* + M \rightarrow C_2H_6 + M \qquad 11.$$

All investigations are based principally on the measurement of ethane/methane ratios in the photolysis of acetone where, at the temperatures used, methane is produced exclusively by $CH_3+CH_3COCH_3 \rightarrow CH_4+CH_2COCH_3$ (reaction 12) and ethane by reaction 8. Lifetime measurements are made by the chopped light method. Kistiakowsky & Roberts (6) have remeasured the high pressure rate constant, $k_8 = k_9$ as 3.7×10^{13} cc. mole^{-1} sec.$^{-1}$ at 440°K., in agreement with earlier results; for CD_3, the rate is the same indicating that $C_2H_6^*$ is a "loose" complex. The expected decrease of k_8 (experimentally, of course, $k_8^{1/2}/k_{12}$) with pressure occurs below 10 mm., and for acetone as M, (k_{10}/k_{11}) is given as 4.5 mm. at 453°K. and 2.7 mm. at 513°K. The only fly in the ointment is that this temperature coefficient is in the wrong direction. Carbon dioxide is much less effective than acetone as a third body. Dodd & Steacie (7) have made a more detailed study of the pressure dependence of k_8. They give values of k_{10}/k_{11} of 6.7×10^{-8} mole cc.$^{-1}$ (1.9 mm.) at 450°K. and 11×10^{-8} mole cc.$^{-1}$ at 520°K. If k_{11} is a collision number, $k_{10} \cong 6 \times 10^7$ sec.$^{-1}$ at 520°K. The relative efficiencies of various gases for energy transfer in reaction 11 are argon, <0.03; CO_2, 0.03; C_4F_{10}, 0.2; $C_6F_{11}CF_3$, 0.3; C_6H_6, 1.0; CH_3COCH_3, 1.0; CH_3CHO, 3.0.

It is now clear that the measurements of k_8 by Ingold & Lossing (8) pertain to the low pressure region, and the observed negative temperature coefficient is due to the positive temperature coefficient of k_{10}, as expected on the basis of Rice-Kassel-Slater type theories.

With respect to the reactions $I+I+M \rightleftharpoons I_2+M$ (reactions 13, 14) Christie, Norrish & Porter (9) report that, contrary to earlier beliefs, in the

flash photolysis of argon-iodine mixtures, I_2 molecules are a very efficient third body, and that $k_{13}^{I_2} = 9 \times 10^{11}$ liter^2 mole^{-2} sec.$^{-1}$, whereas $k_{13}^{(argon)} = 3.1 \times 10^9$, as compared to values of about 4×10^9 given by several authors previously. Britton, Davidson & Schott (10) studied the dissociation reaction (reaction 14) for argon and nitrogen as M by a shock wave method. Final temperatures were in the range 1066 to 1860°K., and reaction times were 30 to 300 μsec. The values of k_{13} were computed and compared to the room temperature flash photolysis values; the most significant result is that k_{13} decreases with temperature, approximately as $(1/T)^{1.5}$.

All gas kinetic studies like those discussed above in which a rate-determining step is an energy transfer process, essentially provide information about the loss of a small amount of vibrational energy by a highly excited molecule. Ultrasonic absorption, impact tube experiments, and other hydrodynamic measurements usually pertain to the de-excitation of the first or second vibrational quantum states by collision. As expected from the theoretical treatment by Zener (11), the former process usually has a high probability, but the latter process may have a low probability when the transfer of a high energy quantum is involved. The present theoretical and experimental position with regard to unimolecular reactions was reviewed at a conference in England (12). The pertinent data on unimolecular reactions are in qualitative agreement with the proposal that deactivation occurs upon every collision between complex molecules, but somewhat less often for simple deactivating molecules [Pritchard, Sowden & Trotman-Dickenson (13)].

It is gratifying to note that improved theoretical prediction of vibrational deactivation probabilities for the second type of process discussed above can now be made for simple molecules which interact only by van der Waals forces [Schwartz & Herzfeld (14)]. Brout (15, 16) has treated the rotational relaxation times of diatomic molecules theoretically, and has been able to account for the low probability of rotational energy transfer in hydrogen. The studies by Amdur *et al.* (17, 18) on high energy scattering processes for neutral molecules provide information about the intermolecular potential function at short distances which will be of value in computing vibrational relaxation probabilities.

Ubbelohde *et al.* (19, 20) have studied ultrasonic dispersion in mixtures of ethylene with other gases and have reported on the number of collisions required to deactivate vibrationally excited ethylene: air, 5000; helium, propane, and ethylene, 2500; D_2 and H_2, 250; H_2O, 85; and for some pentanes and hexanes, 30 to 50. The high transfer efficiency of the flexible larger hydrocarbons is attributed to "wrestling" collisions. A relation between energy transfer and diffusion coefficients is proposed by Ubbelohde & Cummings (21).

Volman (22) has investigated the 2537 Å sensitized formation of ozone from oxygen in the presence of mercury. The quenching effects strongly support the mechanism $Hg^* + O_2 \rightarrow Hg + O_2^*$ (reaction 15), $O_2^* + M \rightarrow O_2 + M$

(reaction 16), $O_2^* + O_2 \rightarrow O_3 + O$ (reaction 17), with relative rate constants for the quenching reaction (reaction 16), of CO_2, 1; A, 0.6; N_2, 0.6; He, 0.05, in general agreement with other energy transfer rate constants of these gases. Various other photosensitisation studies are reported in other sections of this review. Darwent *et al.* (23, 24) have continued their studies of the effect of structure in the quenching of mercury resonance radiation. Increasing molecular weight, branching in the saturated hydrocarbons, substitution with halogens (other than fluorine) and with oxygen, nitrogen, and sulfur, and double bonds all augment the quenching. The quenching cross sections of hydrogen and deuterium for potassium resonance radiation have been measured by Smith, Stuart & Taylor (25); the lighter isotope is the more efficient.

Bowen (26) has studied fluorescence quenching for anthracene and several derivatives in solution and in the vapor. Self-quenching and quenching by NO or by O_2 occur in a high proportion of molecular collisions. The quenching efficiency of various molecules for anthracene increases with falling temperature, as expected if van der Waals interactions are important [Metcalf (27)].

Reactions of Simple Molecules

Harteck & Dondes (28) have estimated that the rate constant of the reaction $O + N_2 + M \rightarrow N_2O + M$ (reaction 18) is $2 \times 10^{-33} \exp(-12{,}000/RT)$ $atom^{-2}$ $cc.^2$ $sec.^{-1}$ from the known thermodynamic heat, the activation energy for the reverse process, and a plausible pre-exponential factor. This leads to the estimate that at +295°C. in a 1:1 N_2, O_2 mixture containing 2.5 per cent O_3, 10^{-4} of the decomposing O_3 should give N_2O; this estimate was confirmed by a preliminary experiment. There are few or no other examples of homogeneous reactions of the nitrogen molecule at such a low temperature. The same authors (29) report that neutron irradiation of NO_2 produces some N_2, O_2, and N_2O, which they attribute to the reactions: $NO_2 + N \rightarrow N_2O + O$ +43 kcal. (reaction 19), $NO_2 + N \rightarrow N_2 + O + O + 3.5$ kcal. (reaction 20) and $NO_2 + N \rightarrow N_2 + O_2 + 120.7$ kcal. (reaction 21).

Aymonino, Sicre & Schumacher (30) have found that from −46° to −26°C., the synthesis of $FClO_2$ from F_2 and ClO_2 is first order in each reagent; they propose the reaction scheme: $F_2 + ClO_2 \rightarrow F + FClO_2$ (reaction 22), followed by $F + F \rightarrow F_2$ (wall) (reaction 23), with some contribution by $F + F + M \rightarrow F_2 + M$ (reaction 24), and $F + ClO_2 \rightarrow FClO_2$ (reaction 25). This last reaction is stated to have a considerable heat of activation, and for the homogeneous reaction, (reaction 22), $k_{22} = 3 \times 10^7 \exp(-8500/RT)$ liter $mole^{-1}$ $sec.^{-1}$, so that the steric factor is quite small.

McDonald, Kahn & Gunning (31) have investigated the photolysis of ammonia at 1849 Å in a flow system at pressures of 1 to 760 mm. The fraction of the ammonia decomposed that forms hydrazine increases markedly with flow rate, but is independent of total pressure. The quantum yield of ammonia decomposition is independent of pressure (and is believed to be about

0.25) in the range of 560 to 100 mm., but increases to about double this value at 10 mm. Although some features are still unclear, it appears that the main reactions are $NH_3+H \rightarrow NH_2+H_2$ (reaction 26) $2NH_2 \rightarrow N_2H_4$ (reaction 26a), $2H \rightarrow H_2$ (walls) (reaction 26b); at low flow rates, N_2H_4 is decomposed both by the incident radiation and by the free radicals present.

Garvin (32) has investigated the thermal reaction between CO and O_3 at 430 to 565°K. in a flow system with contact times of a few tenths to a few seconds. The rate law for the thermal decomposition of ozone in the presence of excess oxygen established by Wulf & Tolman at lower temperatures, $-d(O_3)/dt = k(O_3)^2/(O_2)$, was confirmed and the two sets of rate constants give the same log k versus $1/T$ curve. In the presence of equal amounts of CO and O_3, the rate of CO_2 production is one or two orders of magnitude slower than the thermal decomposition of ozone. The rate law indicates that CO is oxidized exclusively by a termolecular reaction with an oxygen atom and a third body.

$$M + O_3 \rightleftharpoons M + O_2 + O \qquad 27, 28.$$

$$O + O_3 \rightarrow O_2 + O_2 \qquad 29.$$

$$O + CO + M \rightarrow CO_2 + M \qquad 30.$$

Reaction 30 has no activation energy and it is estimated that k_{28}/k_{30} is between 10^2 and 10^3. This result argues against any direct reaction between carbon monoxide and ozone as either a chain breaking or chain diverging step in CO, O_2 explosions. However, as emphasized by the author, the experimental accuracy is not high, and although it is unlikely, it is not impossible that there is a direct reaction between carbon monoxide and ozone at higher temperatures.

By working at low temperatures (−43° to −75°C.) and high dilutions, Johnston & Crosby (33) have succeeded in observing the rate of the reaction, $NO+O_3 \rightarrow NO_2+O_2$ (reaction 31), in a fast mixing, spectrophotometer experiment. The reaction proceeds by the elementary step written above, with $k_{31} = 0.8 \times 10^{12} \exp(-2500/RT)$ cc. mole^{-1} sec.$^{-1}$. The authors tabulate the pre-exponential factors for a series of bimolecular atom transfer reactions involving nitrogen oxides of similar complexity; in all cases, they are in the range of 0.5 to 10×10^{12}.

Graven & Long (34) have investigated the two opposing reactions: $H_2+CO_2 \rightleftharpoons H_2O+CO$ (reaction 32, 33), in a flow system at 900°C., with a residence time of ca. 0.5 sec. The extent of reaction was limited to about 1 per cent, so that each reaction could be studied in the absence of its reverse. The reactions are homogeneous. The rate laws for the forward and reverse reactions are

$$\frac{d(H_2O)}{dt} = \frac{k(H_2^{1/2})(CO_2)}{1 + A(CO)}; \qquad \frac{d(CO_2)}{dt} = \frac{k(CO)^{1/2}(H_2O)}{(1 + B(H_2))^{1/2}}$$

The rate law seems to call quite naturally for the following mechanism:

		ΔE	
chain cycle	$H + CO_2 \rightleftharpoons OH + CO$	23.8	34, 35.
	$OH + H_2 \rightleftharpoons H + H_2O$	−16.0	36, 37.
	$H_2 + M \rightleftharpoons H + H + M$	104.3	38, 39.
	$H_2O + M \rightleftharpoons H + OH + M$	120.3	40, 41.

Reactions 38 and 39 initiate and terminate the chain cycle for the forward reaction 32, and 40 and 41 perform this function for the back reaction 33. The mechanism predicts the experimental rate laws. As pointed out by the authors, there are two serious discrepancies in this otherwise very satisfying kinetic investigation. The observed activation energy for the forward reaction is 57 kcal., but on thermodynamic grounds it must be greater than 76 kcal., *i.e.*, $\Delta E_{34}+(1/2)\Delta E_{38}$. The values of k_{35}/k_{36} determined in the forward and reverse reactions are 14 and 0.02, respectively. It seems to the reviewers that these discrepancies are so large as to cast doubt on the applicability of the proposed mechanism to the experimental results.

Nightingale & Crawford (35) report a preliminary value of 5×10^3 cc. mole^{-1} sec.$^{-1}$ for the bimolecular rate constant of the interesting reaction $BF_3+BCl_3\rightarrow BF_2Cl+BFCl_2$ (reaction 42), as studied by a fast mixing technique and a rapid scanning infrared spectrophotometer.

Lipscomb, Norrish & Porter (36) report that ClO can be produced by the flash photolysis of ClO_2, $ClO_2+h\nu\rightarrow ClO+O$ (reaction 43). It disappears by the reaction $ClO+ClO\rightarrow Cl_2+O_2$ (reaction 44) which was previously observed in the study of the flash photolysis of Cl_2 in the presence of O_2. From the changes in intensity of the ClO_2 and ClO absorption spectra, the concentration and extinction coefficient of ClO can be determined, and the absolute rate constant of reaction 44 established as $8.6\text{–}5.7\times10^7$ liter mole^{-1} sec.$^{-1}$, with zero activation energy.

The photolysis of nitrous oxide at 1470 Å and at 1849 Å has been restudied by Zelikoff & Aschenbrand (37). The quantum yields, $\Phi_{N_2}=1.4$, $\Phi_{O_2}=0.50$, $\Phi_{NO}=0.50$ (but pressure dependent), and $\Phi_{N_2O}=1.7$, seem to favor the mechanism $N_2O+h\nu\rightarrow N_2+O$ (reaction 45), $O+N_2O\rightarrow 2NO$ (reaction 46), $O+N_2O\rightarrow N_2+O_2$ (reaction 47), $O+O+M\rightarrow O_2+M$ (reaction 48) as against the mechanism in which the primary photochemical act is $N_2O+h\nu\rightarrow NO+N$ (reaction 49).

It is good news that Groth (38) has resumed photochemical investigations with far ultraviolet radiation. Irradiation with krypton resonance radiation (1235 and 1165 Å) of a mixture of N_2 (200 mm.), H_2 (400 mm.), Kr (20 mm.) in a flow system produced NH_3 and N_2H_4 with quantum yields of 0.03 and 0.11. It must be assumed that the reaction $Kr^*+N_2\rightarrow Kr+N+N$ (reaction 50) occurs, this reaction being energetically possible whatever the heat of dissociation of N_2. Sheehan (39) has contributed the interesting suggestion that a study of the possibility of the reaction $Xe^*+N_2\rightarrow Xe+N+N$ (reaction 51) using the 1470 (8.43 ev.) resonance line of Xe would serve to distinguish between high and low values for the heat of dissociation of nitro-

gen. Devins & Burton (39a) have studied the production of N_2H_4 from NH_3 in an electric discharge. In the photodecomposition of propane by Xe radiation (1470 and 1295 Å) at room temperature, H_2 and propylene are the main products, with smaller amounts of C_2H_6, C_2H_4, C_2H_2, and C_4 or higher hydrocarbons [Groth & Scharfe (40)]. Other workers have shown that the mercury or cadmium photosensitized decomposition of propane below 300° gives principally H_2 and hexane with no propylene, so the mechanisms of the two reactions must be quite different.

Using O_2 highly enriched in $O^{16}-O^{18}$ but not in $O^{18}-O^{18}$, Ogg & Sutphen (41) observed that the "scrambling" reaction $2O^{16}-O^{18} \rightarrow O^{16}-O^{16}+O^{18}-O^{18}$ is accelerated by O_3 and that its rate is much greater than the rate of exchange of O^{18} with the O_3. The mechanism appears to be

$$M + O_3 \rightleftharpoons O_2^* + M \qquad 52, 53.$$

$$O_3^* \rightleftharpoons O_2 + O \qquad 54, 55.$$

Reactions 54 and 55 lead to scrambling, whereas the entire system of four reactions is necessary for exchange. Addition of excess carbon dioxide favors reactions 52 and 53. It appears that the steady-state O atom concentration in O_3, O_2 mixtures is larger than expected from the above reactions, possibly due to energy chains generated by an exothermic step in the decomposition of ozone. Irradiation with ultraviolet light accelerated scrambling, but red light did not.

Free Radical Reactions

Without doubt, the major event in this field is the appearance of the second edition of Steacie's monograph "Atomic and Free Radical Reactions" (42). It will serve as the authoritative reference on gas phase free radical reactions of organic substances. The author has endeavored to cover all of the literature through June, 1953, and some 1954 publications are included. Several of the papers discussed below are also considered by Steacie.

Free radicals occur at a very low steady-state concentration in most reacting systems, so that their physical properties cannot be directly measured. Several workers this year have indicated an interest in the idea of preparing free radicals in rigid media at higher concentrations so that they will have a long lifetime, making it possible to establish their presence and study their physical properties. Norman & Porter (43) have photolyzed CS_2, ClO_2, and various benzyl derivatives, all in solution in rigid organic glasses at liquid nitrogen temperature, and have observed spectra due to CS, ClO, and benzyl. The spectra of the radicals disappeared when the glass melted. In similar experiments using iodine as a substrate, its color disappeared upon irradiation of the glass and reappeared upon melting. Melting of an ethyl iodide glass after irradiation resulted in the formation of molecular iodine, suggesting that ethyl radicals were present in the glass. The work is an important extension of the earlier work of Lewis & Lipkin (44). Mador (44a) has attempted to stabilize the methyl radical at liquid helium temperatures in various matrices and to obtain its infrared spectrum, but these

experiments appear to be inconclusive. Mador & McWilliams (45) have passed HN_3 through an electric discharge and then on to a liquid helium cooled surface and they have also studied the photodecomposition of a frozen hydrazoic acid film. Infrared bands due to ammonium azide and absorption bands at 3500 Å and at 6000 Å, possibly due to NH and NH_2, resulted. Whittle, Dows & Pimentel (46) report an interesting initial investigation on the possibility of trapping free radicals in a suitable matrix by condensation from the vapor phase.

Bromination is an important topic in chemical kinetics. The hydrogen-bromine reaction was the rock upon which the theory of the kinetics of chain reactions was built. The methane-bromine reaction provides one of the most satisfactory measurements of the H_3C—H bond strength. Unfortunately, a series of further studies of the bromination of hydrocarbons has given anomalous results, as noted below. It is evident from perusal of the experimental details that the investigations have been carried out with admirable care. It is to be hoped that there will be further work which will clear away the difficulties.

Eckstein, Sheraga, & Van Artsdalen (47) have investigated the photochemical and thermal bromination of isobutane (tBuH), and have reviewed and summarized their previous studies on other hydrocarbons. Infrared analysis confirms the expectation that the main product is *t*-butyl bromide (tBuBr), with some 1,2-dibromo-2-methyl propane, which presumably results from further bromination of tBuBr. The kinetics are in accord with the expected chain mechanism.

$$Br_2 \longrightarrow 2\ Br \text{ (thermal or photochemical initiation)} \qquad 56.$$

$$Br + Br + M \longrightarrow Br_2 + M \qquad 57.$$

$$tBuH + Br \rightleftarrows tBu + HBr \qquad 58, 59.$$

$$tBu + Br_2 \longrightarrow tBuBr + Br \qquad 60.$$

The quantitative results are $E_{58}=11.7$ kcal., $A_{58}=3.76\times10^{17}$ cc. mole^{-1} sec.$^{-1}$, $E_{59}-E_{60}=8.0$ kcal., and $A_{59}/A_{60}=10^5$. The assumption that $E_{60}=0$ leads to a value of 89.6 for the tBu—H bond strength. The authors propose that the abnormal steric factor of 2740 for A_{58} is due to the contribution of the energy in four vibrational degrees of freedom to the energy of activation. As is well known, this gives an expression $k=Z(E_0/RT)^{s-1}\exp(-E_0/RT)/(s-1)!$. But it is impossible for energy distributed among several degrees of vibrational freedom to contribute to the activation energy for hydrogen atom transfer along the reaction coordinate of the tBu . . . H . . . Br complex, unless the complex lives long enough for the energy to concentrate in the one bond by a fluctuation process, as in a unimolecular reaction. This lifetime is ca. $(1/\nu)\ (E_0/RT)^{s-1}/(s-1)!\sim10^{-9}$ sec. or greater, which is implausible, to say the least. The very large value of A_{59}/A_{60} is also disturbing.

We believe, as does Steacie (42), that these anomalies cast considerable doubt on the value of the tBu—H bond energy deduced from this investigation. The same anomalies occurred in a previous investigation of the neopen-

tane-bromine reaction (48, 49) which has been criticized on several counts (50, 51). The suggestion (50) that the neopentane anomalies are due to the reaction $(CH_3)_3CCH_2 \rightarrow CH_3 + H_2C=C(CH_3)_2$ cannot apply to isobutane, in view of the infrared analysis for the products.

Pritchard, Pyke & Trotman-Dickenson (52) have measured the relative rates of the reactions $Cl + H_2 \rightarrow HCl + H$ (reaction 61) and $Cl + CH_4 \rightarrow HCl + CH_3$ (reaction 62) by competitive photochlorination over the temperature range 0° to 215°. Assuming $k_{61} = 10^{13.9} \exp(-5500/RT)$ cc. mole^{-1} sec.$^{-1}$, the results are that $k_{62} = 10^{13.4} \exp(-3850/RT)$ cc. mole^{-1} sec.$^{-1}$. The numerical result has been revised in accordance with a private communication from the authors. This method is clearly a very powerful one for the study of the activation energies of chlorine atom reactions, and further work will be awaited with interest. In the present instance, the reviewers wish to point out that the possibilities of hot atom effects have not yet been eliminated; because of the reduced mass situation, these would be more important for CH_4 than for H_2. Furthermore, it should be noted that the rate constant of reaction 61 is really not known accurately.

As usual, there have been a large number of investigations in which an essential reaction has been a hydrogen atom abstraction by a free radical, and we have endeavored to summarize this in tabular form. Because of individual features of each investigation, the table must be supplemented with many notes. Nevertheless, we trust it will assist the reader to view the work as a whole. Further comments on some of the papers are made in the text.

The reader can survey some of the important features of these investigations from the table; for many important details about the temperature range used, analytical techniques, chain terminating reactions, side reactions, and other features he is referred to the original literature. Attention is called to the disagreement between the investigations of references (54) and (55) as to the activation energy of the step $CH_3 + CH_4 \rightarrow CH_4 + CH_3$ (reaction 67). The work of Willard & Harris (55) is noteworthy because of the clear convincing evidence of the occurrence of a hot radical reaction between CH_3 and CH_3I, and for the measurement of its cross section.

Berlie & LeRoy (66) have studied the reaction $H + CH_4 \rightarrow H_2 + CH_3$ (reaction 68) by a flow method in which the hydrogen atom concentration is estimated from the temperature of a metal thermocouple in the gas stream. The results are $E_{68} = 4.5$ kcal., $P_{68} \approx 10^{-5}$. This appears to disagree with the results of studies of the reverse reaction (Table I). It is not clear to the reviewers that the authors have shown that their physical method of detecting hydrogen atoms is quantitatively valid in the presence of other free radicals.

Mandelcorn & Steacie (67) have studied the photolysis of acetone at 100 to 280°C. The most important new point is that methyl ethyl ketone, methane, and ethane together account for 95($\pm$3) per cent of the methyl radicals, and the reaction $CH_3COCH_2 \rightarrow CH_3 + CH_2CO$ (reaction 69) is unimportant in this temperature range. However, McNesby, Davis & Gordon (56) do report ketene formation at 500°C. The two termination reactions involving acetonyl

TABLE I

ATOM ABSTRACTIONS BY RADICALS

Radical	Source	Substrate	E (kcal.)	A (cc. mole^{-1} sec.$^{-1}$) $\times 10^{-14}$ or P(steric factor	Authors
CH_3	$HgMe_2$, $h\nu$	D_2	12.7(±0.5)	—	Rebbert & Steacie (53)
CD_3	$(CD_3)_2CO$, $h\nu$ and pyrolysis	CH_4	14.0	—	McNesby & Gordon (54)
	(By comparison with abstraction from acetone-d_6)				
CH_3	$C^{14}H_3I$, $h\nu$	CH_4	9(±2)	—	Willard & Harris (55)
	(By comparison with CH_3+I_2)				
CH_3	CH_3I, $h\nu$	CH_3I	—	$2.7\times10^{-3}(P)$	
	(Hot radical reaction, wavelength and moderator dependent; CH_3I_2 very susceptible to hot radical attack.)				
CD_3	$(CD_3)_2CO$, $h\nu$	acetone-d_6 versus acetone	E_D-E_H =1.64 (±0.1)	$(A_H/A_D)=0.8$	McNesby, Davis & Gordon (56, 57)
	(Not affected by He, therefore assumed no hot radicals; however He is a poor moderator.)				
CD_3	$(CD_3)_2CO$, $h\nu$	CH_3CN	10(±0.5)	$10^{-3}(P)$	Wijnen (58)
		C_2H_5CN	8.5(±0.5)	$10^{-3}(P)$	
CD_3	$(CD_3)_2CO$, $h\nu$	diethyl ketone	—	—	Wijnen (59)
		DEK (reaction 63)			
		acetone-d_6 (reaction 64)			
		$\frac{k_{63}}{k_{64}}=56.5$ at 141°C.			
CH_3	$(CH_3N)_2$, $h\nu$	DEK	7.0	$7.4\times10^{-4}(P)$	Ausloos & Steacie (60)
C_2H_5	$(C_2H_5N)_2$, $h\nu$	DEK	7.6	$7.1\times10^{-4}(P)$	
C_2H_5	$(C_2H_5N)_2$, $h\nu$	$(C_2H_5N)_2$	7.5	—	Ausloos & Steacie (61)
	(Disproportionation to combination ratio for ethyl is 0.13(±0.02).)				
CH_3	di-*t*-butyl peroxide	acetone	9.5	$6.4\times10^{-3}(A)$	Pritchard, Pritchard & Trotman-Dickenson (62)
	(DTBP)	DTBP	11.7	$25\times10^{-3}(A)$	
	pyrolysis	DEK	8.0	$6.4\times10^{-3}(A)$	
	(Rate of fission of DTBP $=4\times10^{15}$ exp. $(-39{,}000/RT)$ sec.$^{-1}$)				
CH_3	DTBP	$CH_3CH_2\cdot CHO$	7.5	$10^{-3}(P)$	Volman & Brinton (63)
C_2H_5	DTBP	$CH_3\cdot CH_2\cdot CHO$	7.5	$10^{-3}(P)$	
	(C_2H_5 from thermal decomposition of CH_3CH_2CO radicals.)				
CH_3	$HgMe_2$, $h\nu$	3-ethyl pentane	6.8(±0.3)	$1.2\times10^{-4}(P)$	Rebbert & Steacie (64)
CH_3	CH_3COCF_3, $h\nu$	CH_3COCF_3	8.9	$5\times10^{-4}(P)$	Sieger & Calvert (65)
CF_3			6.6	10^{-4}	
	(There is evidence for the reactions $CH_3+CH_3CH_2COCF_3\rightarrow C_2H_6+CF_3CO$ (reaction 65) and $CF_3+CH_3COCF_3\rightarrow CH_4+(CF_3)_2CO$ (reaction 66) at high temperatures.)				

radicals, $CH_3+CH_2COCH_3 \rightarrow MEK$ (reaction 70) and $CH_2COCH_3 + CH_2COCH_3 \rightarrow$ biacetonyl (reaction 71) are both important and have steric factors of the order of unity [Mandelcorn & Steacie (68)]. Above 300°, some ethylene is formed, perhaps due to hydrogen abstraction from methyl ethyl ketone, followed by $C_2H_4COCH_3 \rightarrow CH_3+CO+C_2H_4$ (reaction 72). Rubin & Leach (69) have investigated the photolysis of acetone at room temperature and very low pressures (5 to 100 μ). It is believed that the results show that excited acetyl radicals (CH_3CO^*) are formed with a high probability ($\sim$0.8) in the primary photochemical step, and that they are either deactivated or decompose, $CH_3CO^* \rightarrow CH_3+CO$ (reaction 73).

To explain the formation of 2-butene in the photolysis of *trans*-methyl propenyl ketone, or in the reactions of methyl radicals from acetone or di-*t*-butyl peroxide with this substrate, a new kind of reaction, an "addition-elimination," for methyl radicals has been proposed [Pitts, Tolberg & Martin (70)]:

$$CH_3 + CH_3COC(H)=CCH_3 \rightarrow CH_3CO + CH_3C(H)=CCH_3 \qquad 74.$$

Mandelcorn & Steacie (71) have investigated the photolysis of acetone in the presence of the unsaturated substances, ethylene, propylene, acetylene, and butadiene by studying the effects of these reagents on the production of methane, ethane, and methyl ethyl ketone. Activation energies for methyl addition are found to be 7.0, 6.0, 5.5, and 2.5 kcal., respectively.

Bell & Blacet (71a) have published a detailed account of their work on the photolysis of biacetyl previously reviewed by Robb (71c). Activation energies for the abstraction by methyl from biacetyl of hydrogen and acetyl to give methane and acetone, respectively, are revised to be 7.7 and 6.6 kcal. Quantum yields for the various products at several wavelengths are reported, and the effect of iodine as an inhibitor is discussed. There is evidence of a significant difference in the primary photochemical processes at the two wavelengths. Blacet & Crane (71b) have studied the photolysis of propionaldehyde, *n*-butyraldehyde, and isobutyraldehyde at 2380 and 1870 Å. The quantum yields of the various products are markedly different at the two wavelengths.

Pitts & Norman (71d) have investigated the vapor phase photolysis of methyl cyclopropyl ketone at 2537 to 2654 Å. The primary reaction is a rearrangement to methyl propenyl ketone, with a quantum yield of 0.31 ± 0.02 in the range 25° to 120°C. The probability of dissociation into free radicals appears to be very small.

In the mercury photosensitized decompositions of cyclohexane and cyclopentane, the ratios of recombination to disproportionation for cyclohexyl and cyclopentyl radicals are 2.2 and 5.3, respectively [Beck, Kniebes & Gunning (72, 73)].

Callear & Robb (74) have studied the mercury photosensitized decomposition of ethylene manometrically and by measuring the photostationary temperature gradients; the reaction products are acetylene and hydrogen. The

authors advocate a molecular mechanism: $Hg^* + C_2H_4 \rightarrow Hg + C_2H_4^*$ (reaction 75), $C_2H_4^* \rightarrow C_2H_2 + H_2$ (reaction 76), $C_2H_4^* + 2C_2H_4 \rightarrow 3C_2H_4$ (reaction 77). The termolecular deactivation step is unusual, and several interesting comments as to its mechanism, its reality, or both, were advanced at the Faraday Discussion. Thus, the authors do not believe that this investigation involves free radicals, but it is included here because it is believed by others that all mercury photosensitized reactions of organic substances proceed by a free radical mechanism (75).

Takezaki & Takeuchi (76) have studied the decomposition of methanol induced by CH_3O radicals from pyrolysis of dimethyl peroxide. The rate constant of the reaction $CH_3OOCH_3 \rightarrow 2CH_3O$ (reaction 78) is given as $4.1 \times 10^{15} \exp(-36{,}900/RT)$ sec.$^{-1}$; for the secondary steps, $CH_3O + CH_3OH \rightarrow CH_3OH + CH_2OH$ (reaction 79) and $CH_3O + H_2CO \rightarrow CH_3OH + CHO$ (reaction 80), the activation energy difference is estimated as $E_{79} - E_{80} = 3$ to 4 kcal.

Cvetanovic & Whittle (77) have considered possible errors in interpretation of kinetic data due to the spatial and temporal variation of free radical concentration for various idealized cases.

McCarthy (78) has studied the production of free radicals by microwave discharges.

Bond Dissociation Energies

The contribution which gas kinetics has made to the measurement of bond strengths has been surveyed by Cottrell in his recent publication (79); the limitations and shortcomings are discussed. Since the monograph was prepared, Blades, Blades & Steacie (80) have reported a careful study of the pyrolysis of toluene in a flow system. Their findings differ in many respects from those reported in the earlier work of Szwarc (81). In addition to bibenzyl, a mixture of isomeric dimethyl diphenyls, together with some styrene was found in the products. These are considered to be produced from the participation of benzyl radicals or bibenzyl in secondary reactions, which also produce hydrogen. First-order rate constants calculated from the rate of production of hydrogen plus methane vary somewhat with pressure, with the nature of the surface, and greatly with the contact time. It is proposed that the reaction introduced by Szwarc to explain the production of benzene and methane $H + C_6H_5CH_3 \rightarrow C_6H_6 + CH_3$ (reaction 81) does not, in fact, occur, and instead these products arise from the fission $C_6H_5CH_3 \rightarrow C_6H_5 + CH_3$ (reaction 82) occurring simultaneously with $C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H$ (reaction 83). Hence, the observed activation energy (which is found to be 89 kcal. compared with 77.5 observed by Szwarc) cannot be assigned to a single step, and it is concluded to be premature to assign any definite value to the C—H bond dissociation energy in toluene. The secondary reactions of bibenzyl are confirmed by pyrolysis of the compound in toluene, which results in loss of bibenzyl and the corresponding production of hydrogen and isomeric dimethyl diphenyls.

Summarizing the significance of these findings, Steacie (42) concludes that, although work resulting in the determination of a large number of bond dissociation energies by Szwarc and his co-workers is of great importance, the detailed mechanisms of the processes involved are doubtful, and the results must be considered as "having the character of an excellent preliminary quantitative survey, rather than as well-established detailed investigations."

By pyrolysis of benzyl chloride and bromide in a toluene-flow system, Szwarc & Taylor (82) have deduced the bond energies $D(C_6H_5CH_2—Cl) = 68$ kcal., $D(C_6H_5CO—Cl) = 73.2$ kcal. The latter value leads to 15.7 kcal. for $\Delta H_f(C_6H_5CO)$, in good agreement with 15.6 kcal./mole deduced from the previously determined $D(C_6H_5CO—Br)$. Rembaum & Szwarc (83) have similarly studied the decomposition of gaseous acetyl peroxide over the temperature range 90 to 190°C. The products are mainly CO_2 and C_2H_6 along with a small proportion of CH_4; the molar ratio $(CO_2/(C_2H_6+CH_4))$ is constant at 2. It is concluded that the rate-determining step is $CH_3COO-OOCCH_3 \rightarrow 2CH_3CO_2$ (reaction 84) and that $k_{84} = 1.8 \times 10^{14} \exp(-29{,}500/RT)$ sec.$^{-1}$, so that the O—O bond dissociation energy is 29.5 kcal. Levy, Szwarc & Throssel (83a) have pyrolyzed *p*-xylyl monobromide in toluene over the temperature range 475 to 541°C. The data indicate that the quinonoid hydrocarbon $CH_2{=}C_6H_4{=}CH_2$ is produced by disproportionation of xylyl radicals, rather than by hydrogen elimination; the activation energy of the elimination process is estimated as ~70 kcal./mole. Reinvestigation of the pyrolysis of benzyl bromide confirmed the earlier value for $D(C_6H_5CH_2—Br)$. The rate constant for the decomposition of *p*-xylyl bromide was essentially equal to that for the decomposition of benzyl bromide, and the rate constant for the decomposition of ω,ω'-dibromo-*p*-xylene was higher by a statistical factor of 2 than that for *p*-xylyl bromide.

Page, Pritchard & Trotman-Dickenson (84) have used the toluene-carrier method to reinvestigate the thermal decomposition of azomethane in the range 390 to 450°C. In 15 mm. of toluene, $k = 10^{14} \exp(-46{,}000/RT)$ sec.$^{-1}$ agreeing with results of previous workers in azomethane alone. It is probable that the primary step is the splitting-off of a methyl radical. At all events the high percentage of methane formed dispenses with an earlier proposal that the molecule decomposes directly into C_2H_6 and N_2. Thoretical arguments are presented which show that 46 kcal./mole is not an unreasonable value for the C—N bond strength.

By flow pyrolysis of benzyl mercaptan in toluene, Sehon & Darwent (85) have obtained $D(C_6H_5CH_2—SH) = 53$ (± 2) kcal. Methyl mercaptan decomposes by a complicated free radical mechanism, and ethyl mercaptan by a radical mechanism competing with a molecular split to ethylene and H_2S; consequently the data obtained from these two compounds are considered by the authors to be somewhat ambiguous.

Several papers dealing with bond energies determined by mass spectros-

copy will be of interest to kineticists. Results pertaining to C—H bonds are summarized in Table II.

Lossing, Ingold & Henderson (89) have further measured the appearance potentials of the radical ions from a series of methyl, allyl and benzyl halides, and have deduced the carbon-halogen bond strengths. They present a table of their results and of those in the literature.

TABLE II

C—H Bond Energies from Appearance Potentials

Species	Source	Ionization Potential(ev)	D(C—H) kcal./mole	Authors
CH_3	$(CH_3)_2Hg$, hot Pt filament	10.11±0.10	(78±5)	Waldron (86)
CH_2		—	≤128±9	
CH_3	CH_4 $(CH_3N)_2$, $Pb(CH_3)_4$ heated in quartz tube	9.85±0.1	81(±7)	Langer, Hipple & Stevenson (87)
CH_2		11.7(±0.1)	90(±7)	
CH_4^+		—	30(±2)	
CH_3^+		—	127(±5)	
CH_2^+		—	76(±5)	
CH^+		—	83(±5)	
(appearance potentials of C^+, CH^+, and CH_2^+ lead to 15.5 (±0.5) ev. (358 kcal.) for the heat of atomization of CH_4, and 132 kcal. for the heat of sublimation of graphite.)				
CH_4	$(CH_3)_2Hg$ pyrolysis in He stream		102.8(±1.5)	Lossing, Ingold & Henderson (88)
CH_3		9.95±0.03		
$CH_2CH=CH_2$	$CH_2=CH\ CH_2I$, $CH_2=CH\ CH_2CH_3$ pyrolysis	8.16±0.03	—	
$C_6H_5CH_2$	$C_6H_5CH_2I$ pyrolysis	7.73±0.08	—	

Schissler & Stevenson (90) have measured the appearance potential of the benzyl ion from toluene, ethylbenzene and bibenzyl, and using appropriate thermochemical data obtain 77±3 kcal./mole for $D(C_6H_5CH_2—H)$, in agreement with the flow pyrolysis value of Szwarc (81). However, the result is disputed by Farmer *et al.* (91), who consider that the ionization of benzyl is not a simple process; these authors have observed that in the case of trideuterotoluene, the following reactions occur:

$$C_6H_5CD_3 + e \rightarrow C_6H_5CD_2^+ + D + 2e \qquad 85.$$

$$C_6H_5CD_3 + e \rightarrow C_6H_4CD_3^+ + H + 2e \qquad 86.$$

Field & Franklin (92) have measured the ionization potential of a number of aromatic hydrocarbons by electron impact. The implications of the results are discussed at length, especially with regard to theoretical calculations and to reaction mechanisms involving carbonium ions in solution. The heats of formation of phenyl and ethyl phenyl radicals are deduced as approximately 66 and 49 kcal./mole, respectively.

General Pyrolyses

A substantial amount of work has been reported on the pyrolysis of organic molecules, both in static and in flow systems. In some cases, the reactions involved are simple and unambiguous, and the results lead to valu-

TABLE III

Bond Energies (kcal./mole)

Compound	CH_3—I	CH_3—Br	CH_3—Cl	CH_3—F	CH_3—OH	allyl—I
Work of L.I.H.	50.7±1.5	66.4±2	80.5±3	107±12	91.1±4	34.1±1.5
Literature	55	67.4	80.7	—	91.2	~34.4

Compound	allyl—Br	allyl-Cl	$PhCH_2$—I	$PhCH_2$—Br	$PhCH_2$—Cl
Work of L.I.H.	47.7±2.5	60.4±3	34.6±3	44.7±3	60.4±4
Literature	~45.5	~59.3	~36.5	~48.5	

able data on energies, entropies, and mechanisms of reactions. In other cases, overall reactions are complex and include radical-chain processes; interpretation of the data must then be highly tentative.

Chilton & Gowenlock (93) have studied the pyrolysis of di-isopropyl mercury in a flow system, using both nitrogen and a mixture of nitrogen and nitric oxide as carrier gases. Mercury alkyl pressures were about 0.1 mm., nitrogen pressures between 3.4 and 7.6 mm. The overall mechanism proposed (in the absence of NO) is

$$\text{Hg (iso-Pr)}_2 \rightarrow \text{Hg} + 2\ \text{iso-Pr} \qquad 87.$$

$$\text{iso-Pr} + \text{iso-Pr} \begin{cases} \rightarrow \text{C}_3\text{H}_6 + \text{C}_3\text{H}_8 & 88. \\ \rightarrow (\text{CH}_3)_2\text{CH CH}(\text{CH}_3)_2 & 89. \end{cases}$$

and at 3.7 mm. total pressure, $k_{87} = 10^{15.63} \exp(-39{,}300/RT)$ sec.$^{-1}$. Variation of the ratio of C_6 to C_3 hydrocarbons with total pressure is attributed to "third-body" effects in reaction 89. This is conceivable on account of the low efficiency of nitrogen in energy transfer (13). However, the ratio also varies with contact time, and no explanation of this can be offered. The same authors (94) have studied the pyrolysis of di-*n*-propyl mercury under essentially the same conditions. For the step $Hg(n\text{Pr})_2 \rightarrow Hg + 2n\text{Pr}$ (reaction 90), $k_{90} = 10^{15.52} \exp(-47{,}100/RT)$ at 4.4 mm. total pressure.

From the activation energy and appropriate thermochemical data a value of approximately 98 kcal. is derived for $D(n\text{Pr—H})$. The fate of *n*-propyl is considered to involve, in addition to steps analogous to reactions 88 and 89, decomposition to give methyl and ethylene, and combination with methyl to give *n*-butane. In a further communication (95) the authors report a continuation of their very valuable work on the reaction of nitric oxide with free radicals. Di-*n*-butyl mercury was pyrolyzed in a nitrogen-nitric oxide flow system, and the products were found to consist mainly of nitrosoethane and acetaldoxime; the principal reaction was therefore with ethyl radicals produced by decomposition of butyl. The dimerization of nitroso-alkanes is discussed, and an earlier proposal of a rapid isomerization to oximes at room temperature is considered to be incorrect.

Blades (96) has continued his work on the pyrolysis of esters. Ethyl formate, isopropyl formate, ethyl acetate and isopropyl acetate were decomposed to the corresponding acid and alkene in a toluene flow system at temperatures betwen 440° and 920°C. The reactions are predominantly homogeneous and free from chains. The four rate constants are 2.1×10^{11} exp $(-44{,}140/RT)$, 3.8×10^{12} exp $(-44{,}000/RT)$, 3.1×10^{12} exp $(-47{,}750/RT)$, and 1.0×10^{13} exp $(-45{,}000/RT)$ sec.$^{-1}$, respectively. The low frequency factors are in accord with a cyclic transition state. In a static system, *t*-butylamine has been pyrolyzed over the temperature range 498° to 541°C. [Pritchard, Sowden & Trotman-Dickenson (97)]. The molecule undergoes two simultaneous "molecular splits"

$$CMe_3NH_2 \rightarrow Me_2C{=}CH_2 + NH_3 \qquad 91.$$

$$CMe_3NH_2 \rightarrow C_3NH_7 + CH_4 \qquad 92.$$

and the overall reaction is homogeneous and free from chains. The activation energies of reactions 91 and 92 differ by not more than 1 kcal., and the overall rate constant is $10^{14.79}$ exp $(-67{,}000/RT)$ sec.$^{-1}$. The pre-exponential factor is unusually large for this type of reaction.

The widespread occurrence of radical chain reactions in thermal decompositions is now well established. It has become a practice in recent years to suppress chains by adding one of a number of inhibitors; any reaction occurring when addition of inhibitor ceases to be effective is assumed to be a nonchain process. The dangers and uncertainties inherent in such a simple interpretation are discussed by Steacie (42). Crawford & Steacie (98) have shown that in the pyrolysis of *n*-butane, the data obtained in the presence of nitric oxide were not reproducible. Moreover, Rice & Varnerin (99, 100) have examined the decompositions of ethane and acetaldehyde in the presence of fully deuterated indicators, and of ethane-d_6 and acetaldehyde-d_4 in the presence of undeuterated indicators. They report isotopic mixing even under conditions of "maximum inhibition" with NO and propylene, and conclude that these decompositions proceed entirely by Rice-Herzfeld free radical mechanisms. Evidently, conclusions drawn from experiments involving "partial inhibition" should be regarded as highly speculative.

Hinshelwood and his school have continued their extensive and interesting studies on paraffin hydrocarbon decompositions, and papers have appeared which confirm and strengthen earlier experimental data. Danby *et al.* (101) and Spall, Stubbs & Hinshelwood (102) have carried out mass-spectrometric analyses of products arising from the nitric oxide inhibited decomposition of *n*-pentane. Rates of production of methane, propene, and ethylene are shown to be linear functions of pressure change over a wide variety of temperatures, pressures, and percentages of reaction; it is claimed that this dispenses with the possibility of the observed kinetic anomalies being due to nonlinearity of the pressure-reaction relationship. Jach, Stubbs & Hinshelwood (103) have studied the effects of the three inhibitors nitric oxide, propylene, and isobutene on the decompositions of *n*-pentane, isopentane, and isobutane. For a given paraffin, the same limiting rate is produced by each of the inhibitors. This is considered to argue strongly in favor of the residual reaction being a direct molecular decomposition, and not an imperfectly suppressed chain. Spall *et al.* (104) have further examined the nitric oxide inhibited decomposition of *n*-pentane. The production of ethane (reaction 93) tends to be replaced by production of ethylene and hydrogen (reaction 94) as the pressure is lowered.

$$C_5H_{10} \rightarrow C_3H_6 + C_2H_4 \qquad 93.$$

$$C_5H_{10} \rightarrow H_2 + 2C_2H_4 \qquad 94.$$

This is considered to support the hypothesis of a change with pressure in the predominant mode of activation of the molecule. The hypothesis is discussed fully by Spall, Stubbs & Hinshelwood (102), and the double change in order between first and second as the pressure is decreased is interpreted in terms of a theory of two modes of activation. However, Johnston & White (105), have pointed out that such an interpretation is not permitted by a Lindemann-type theory of unimolecular reactions, for regardless of the number of modes of activation in operation, a curve of first-order rate constant versus pressure may never have a point of inflection. Hence, the class of inhibited decompositions described by Hinshelwood and his collaborators as exhibiting this behavior must be considered complex. It is also doubtful whether the "residual reactions" exhibiting a single order transition are simple unimolecular reactions. The experiments by Rice & Varnerin (100) described above show that ethane, which falls in this class, almost certainly decomposes by a Rice-Herzfeld mechanism at maximum inhibition.

Howlett has made further studies of the pyrolysis of chloroalkanes. Goodall & Howlett (106) report that the decomposition of allyl chloride in the temperature range 370°-475°C. is complex, and includes simultaneous chain, nonchain and heterogeneous processes. The same authors have examined the decomposition of trichloroethylene in the range 385° to 445°C. (107); they consider the residual reaction after suppression of chains with either propylene or *n*-hexane to be a molecular decomposition into hydrogen chloride and dichloroacetylene. This appears to be second-order up to 50

mm. pressure, which would support Slater's prediction (108) that unimolecular decompositions of small molecules will be in the second-order region in this range. However, in view of the complexities involved, the work cannot be considered as conclusive.

Cullis & Priday (109, 110) have pyrolyzed chlorobenzene and the isomeric dichlorobenzenes in a silica vessel within the range 700° to 800°C. In the case of chlorobenzene, approximately one mole each of hydrogen chloride and hydrogen are produced for every mole of chlorobenzene decomposed; the remaining hydrogen is contained in a carbonaceous layer deposited on the walls of the reaction vessel. The rate of decomposition is lowered to the same limit by the addition of ammonia and nitric oxide. The dichlorobenzenes, on the other hand, produce little gaseous hydrogen, and the rate of production of HCl is unaffected by NH_3 and NO. It is suggested that the inhibited reactions may involve a direct unimolecular fission to give HCl, though the experimental data do not permit rigorous conclusions about the mechanism to be drawn.

Bernstein (111) has made an interesting study of the C^{12}-C^{13} fractionation factor in the decomposition of nickel carbonyl. Previous work indicates that the rate-determining step is the rupture of a nickel-carbon bond,

$$Ni(CO)_4 \rightarrow Ni(CO)_3 + CO \qquad 95.$$

$$Ni(CO_4)C^*O \begin{cases} \rightarrow NiCO_3 + C^*O & 96. \\ \rightarrow Ni(CO)_2C^*O + CO & 97. \end{cases}$$

By measuring the C^{12} enrichment of the first CO fraction, it was found that over the range 30° to 105°C.

$$k_{96}/(k_{96} + k_{97}) = 1.0222 - 6.7 \times 10^{-5}\, T(°C.)$$

Assuming the intramolecular effect $k_{97}/3k_{96}$ to be the square root of the reduced mass ratio, the intermolecular effect is

$$k_{95}/4k_{96} = 1.0481 - 6.7 \times 10^{-5}\, T(°C.)$$

A calculation using the method of Bigeleisen (112) shows that this effect is larger than the theory would predict.

Das *et al.* (113) have investigated the homogeneous thermal decomposition of cyclobutanone over the range 333° to 373°. It proceeds essentially by a molecular fission to ethylene and ketene as the primary products, with first-order kinetics from 10 to 88 mm. at 368°, and $k = 3.6 \times 10^{14} \exp(-52{,}000/RT)$ sec.$^{-1}$. No inhibition was observed on adding propylene, toluene, and nitric oxide. Investigation of the reaction at lower pressures was unfortunately prevented by heterogeneous complications. The homogeneous thermal decomposition of cyclopentanone which yields principally (*a*) 2-cyclopentene-1-one and H_2, and (*b*) butene-1 and CO; has an induction period and is not kinetically simple [Johnson & Walters, (114)].

Levy (115) has carried out a thorough reinvestigation of the decomposition of ethyl nitrate over the temperature range 161–201°C., using infrared

and visible spectral analysis. The final products consist mainly of ethyl nitrite, NO and NO_2. The reaction is found to be complex, and attempts to interpret previous manometric studies in terms of a rate determining step are shown to be without foundation. The mechanism proposed is

$$C_2H_5ONO_2 \rightleftharpoons C_2H_5O + NO_2 \text{ (reaction 98, 99)}$$
$$C_2H_5O \rightarrow CH_3 + CH_2O \text{ (reaction 100)}$$

followed by reactions of CH_3 and CH_2O with NO_2, producing NO which further reacts

$$NO + C_2H_5O \rightarrow C_2H_5ONO \text{ (reaction 101)}$$

This mechanism is substantiated (116) by a study of the effect of additives. NO_2 inhibits the decomposition by accelerating reaction 99, and oxygen causes inhibition by oxidation of NO. Addition of ethyl nitrite is without effect, while addition of NO increases the rate to a limiting value via reaction 101. Examination of the effect of diethyl peroxide eliminates the step

$$C_2H_5O + C_2H_5ONO_2 \rightarrow C_2H_5OH + CH_3CHONO_2 \text{ (reaction 102)}$$

proposed in an earlier mechanism. In the light of these facts, the author has isolated the primary process (reaction 98) by studying the decomposition in the presence of NO and acetaldehyde, which remove ethoxy radicals and NO_2, respectively. It is found that $k_{98} = 10^{16.85} \exp(-41{,}230 \pm 495/RT)$ sec.$^{-1}$; the C_2H_5O—NO_2 bond strength is thus 41 kcal./mole, and the entropy of activation about 15 cal./mole degree.

Miscellaneous

There has been a Faraday Society Discussion on "The Study of Fast Reactions" (120), in which the emphasis was principally upon a review of modern experimental techniques. Kinetic results for particular reactions that were reported therein have been dealt with where appropriate throughout the present review.

In a timely article, Robb (121) has proposed a logical and unique definition of rate constant; his suggestion is that the rate constant refer to the stoichiometric equation for the formation or disappearance of one mole (or molecule) of the transition state complex. Theoretical calcuations almost invariably involve the rate constant in this form.

Benson (122) has carried out some interesting calculations on temperature gradients in closed reacting systems. He deduces that in a normal sized vessel under conditions commonly encountered, the average temperature difference between the walls of the vessel and the gas they enclose may be of the order 2° or greater, leading to an error in the determination of absolute rate constants.

Clark, Pritchard & Trotman-Dickenson (123) have investigated the exchange of labelled I atoms between I_2 and CH_3I in an attempt to obtain data on the simplest type of Walden inversion. In a static system over the temperature range 180° to 375°C. the reaction followed the rate law $R = k[MeI]$

$[I_2]^{1/2}$, but was largely heterogeneous. A lower limit of 32.2 kcal. was deduced for the activation energy of the homogeneous exchange.

Cashion & Leroy (124) report a study of the reactions of hydrogen atoms with acetylene; the atoms were produced by mercury photosensitization. The overall reaction is very complicated, and the proposed radical mechanisms are of necessity highly speculative. Onyszchuk, Breitman & Winkler (125) have studied the reaction of active nitrogen with propane, and Back & Winkler (126) its reaction with the butanes. All interpretation of results is based upon the very uncertain assumption that the active species is atomic nitrogen.

The combination of ethylene with diborane yielding boron triethyl as a final product proceeds in the range 120° to 175° at a rate given by $-dp/dt = k[B_2H_6]^{3/2}/(1-a[B_2H_6]/[C_2H_4])$ [Whatley & Pease (127)]. The rate-determining process in the mechanism is considered to be the formation of the intermediate B_3H_9,

$$B_2H_6 \rightleftharpoons 2BH_3 \qquad 103, 104.$$

$$BH_3 + B_2H_6 \rightarrow B_3H_9 \qquad 105.$$

followed by the rapid reaction

$$B_3H_9 + C_2H_4 \rightarrow B_2H_5(C_2H_5) + BH_3 \qquad 106.$$

In a similar way, molecules like $B_2H_5(C_2H_5)$ add on BH_3 and then become further ethylated. It is suggested that the explosive term in the denominator is due to reactions like

$$B_3H_7(C_2H_5)_2 + B_2H_6 \rightarrow B_2H_5(C_2H_5) + B_2H_5(C_2H_5) + BH_3 \qquad 107.$$

which effectively introduce another molecule of B_2H_6 into the sequence of rapid ethylation reactions.

Adams, Bernstein & Katz (128) have made a study of the isotope exchange reactions of radio-fluorine with chlorine trifluoride, bromine pentafluoride, and iodine heptafluoride, using a nickel reaction vessel in the temperature range 181° to 257°C. The exchanges are found to be principally heterogeneous under these conditions.

Oxygenation Reactions

The reviewers regret that limitations of space prevent a proper consideration of papers devoted to this topic, including a study of the photochemistry of ketene-oxygen mixtures [Strachan & Noyes, (129)], the photooxidation of acetone [Christie (130); Hertz (131); Hoare (132)], the combustion of cyclopropane [Broatch, McEwan & Tipper (133)], the oxidation of CO [Hoare & Walsh (134)], of *n*-butane [Quon, Lana & Govier (135)], and of propylene [Muleahy & Ridge (136)].

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SURFACE CHEMISTRY AND CONTACT CATALYSIS

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Introduction.—The literature survey for this review was completed late in December, 1954. Papers published in 1954 and late in 1953 are included. If there is any general trend in the field, it is a gratifying appearance of rigor, both experimental and theoretical, in the best papers. Perhaps this is due to the current intensification of interest in surfaces shown by calorimetrists and solid-state specialists.

Volume I of the treatise on catalysis edited by Emmett (1) appeared during the year. It is devoted to a survey of basic topics. Future volumes are to cover the more technical aspects of the subject. Volume VI of *Advances in Catalysis* includes a lengthy discussion of recent Japanese work by Kwan (2). Also, there is a long-overdue discussion of the interpretation of measurements made over the usual porous catalyst, by Weisz & Prater (3). Most of the article is devoted to effects produced by diffusion. Bond (4) has reviewed the hydrogenation-of-ethylene reaction.

Heat capacity of small particles.—At sufficiently low temperatures, the heat capacity of a finely divided solid would be expected to differ from the heat capacity of the corresponding large crystal, because of the limitations on the wavelengths of the acoustical modes of vibration imposed by the small dimensions of the powder particles, and the thermal motions of the particles with respect to each other. Dugdale, Morrison & Patterson (5) have made extremely careful measurements on rutile powders of widely varying surface area, and fail to find this effect in the liquid hydrogen range where they had expected it. Instead, there does exist a high-temperature effect dependent on particle size which can be described as an optical mode, with an Einstein frequency characteristic of vibration in the surface. Since the low-temperature effect was expected to amount to at least six per cent at 20°K. for the largest surface used, its absence is quite puzzling. The authors intend to extend the measurements to the liquid helium range; even if an effect is found there, a discrepancy with theory remains.

Phase transitions.—The possible existence of two-dimensional phase transitions has continued to stimulate interest. One person, at least, has solved the problem by asserting that such a transition is thermodynamically impossible (6). It is certainly true that, if one considers that the surface is inevitably slightly distorted by the growth of an island of condensed adsorbate, that the gas pressure will change slightly as the island grows. However, a similar argument will prove that bulk condensation into a finite vessel will take place over a slight range of pressure. It would appear that, at least under favorable circumstances, this distortion effect would be of negligible magnitude. A more practical reason to doubt the appearance of a

phase transition on the surface of the solid is the presence of crystal edges and frozen defects. The whole question becomes an academic one, however, when one realizes that it is not possible to verify experimentally the exact criterion for a first-order transition. All that one can assert is that the isotherm exhibits a pronounced point of inflection which could possibly be represented as a step.

Ross & Winkler (7) report a number of crystalline surfaces which show stepwise isotherms with ethane at 90°K. On calcium fluoride, the series observed is reminiscent of the classical isotherms of Jura *et al.* (8). It appears that ethane has nearly optimum properties for showing steps at liquid oxygen temperatures. Argon does not interact strongly enough with its neighbors while, on the other hand, heptane is so strongly adsorbed that it is difficult to be assured of equilibrium. Measurements at a number of temperatures enabled Ross & Clark (9) to calculate the isosteric heat of adsorption of xenon, methane, and ethane on the {100} plane of sodium chloride. All one can say is that their results are logically explained by two-dimensional condensation, with a critical temperature somewhat lower than one-half the bulk value for the adsorbent. An attempt to rationalize this temperature is made on the basis of a modified two-dimensional van der Waals equation. One must be cautious in accepting this treatment, because the equation is certainly invalid when it is applied to critical phenomena. In a further paper (10), these authors investigate the complex behavior of diborane on sodium chloride.

A system which does, or does not, show "first-order transition," depending on the arrangement of the sample bulb, has been reported by Corrin & Rutkowski (11). The higher isotherm for the adsorption of krypton on "a calcium halophosphate," obtained by taking twelve-hour points with the sample on a series of trays, was continuous. In a cylindrical bulb without trays, the system appeared to come to equilibrium in two hours and yielded a discontinuous isotherm. Unfortunately, no desorption points are reported, so therefore, it is impossible to say which, if either, of the isotherms is at equilibrium, or metastable. One thing is clear, however; when the gas pressure is in the micron range, adsorption studies may yield spurious results. When one considers that many chemisorption data fall in this range it is not surprising that that field is so full of anomalous and contradictory findings.

Multilayer adsorption.—The heats of adsorption on a series of heat-treated carbon blacks prepared by Polley, Schaeffer & Smith (12) have been measured by Beebe & Young (13). As the temperature of preheating is raised by intervals from 1000°C. to 2700°C., a maximum in the heat of adsorption near a monolayer develops and sharpens. Concomitantly, the initial heat declines, and begins to rise with coverage, rather than fall. These effects are exactly what one would expect if the surface were initially heterogeneous and became more homogeneous as it is heated. It is clear, however, that even at the highest temperature, the carbon is far from completely uniform.

On a completely uniform surface, the heat of adsorption will be a set of descending stair-steps, corresponding to the completion of each layer. It will exhibit no maximum or, more exactly, "hump."

The series of isotherms on calcium fluoride reported by Edelhoch & Taylor (14) exhibit a wide variety of behavior. Nitrogen and carbon monoxide are strongly adsorbed in the typical type II manner. If there is any phase transition, it is hidden by the low pressure maintained until the monolayer is complete. However, rough isosteric heats indicate that the surface is heterogeneous enough towards these isoelectronic gases to wipe out the effect of interaction. With oxygen and argon, points of inflection indicate cooperative interaction and, for argon, the onset of possible two-dimensional condensation is observed. These gases are adsorbed less strongly and, apparently, the surface appears more homogeneous to them. In the cases of xenon and propane "point B" disappears, and the isotherms become type III. In this paper, also, the theoretical treatment of a two-dimensional condensation is at best shaky.

The heat of adsorption of argon on graphite has been measured by Crowell & Young (15) by the use of the Clausius-Clapeyron equation on the isotherms measured between 80° and 90°K. After the usual initial decline from higher values below 0.2 monolayer the heat is roughly constant at 2.8 kcal., until a slight maximum is encountered at the monolayer. It then declines slowly toward the heat of sublimation of argon. The layer structure of graphite makes a computation of the heat by theoretical means particularly appropriate for two reasons; only one face is presumed to be exposed, and the distance between basal planes makes the contribution from all but the first two quite small. The authors use the method due to Lennard-Jones and employ the Kirkwood-Müller formula to determine the absolute magnitude of the van der Waals forces involved. They calculate the minimum in the energy of interaction over three contrasted lattice positions. They find that all three give about 1.7 kcal. and therefore conclude that motion over a graphite surface by an argon atom can occur without encountering any appreciable energy barrier. Thus, a pure graphite surface should be ideally uniform in the sense that it should be possible to write a two-dimensional translational partition function for the motion of argon over the surface. Young (16) has pulverized potassium chloride, measured isotherms over a range of temperature, and then computed the heat of adsorption as a function of coverage. Since the heat curves are known for the pure {100} and {111} faces, it was possible to compare the three curves. After 0.2 of a monolayer the heat was roughly like that on the {100} face. It was therefore concluded that 20 per cent of the surface was composed of higher-index faces, and thus contributed a "heterogeneity."

In a study of the validity of BET-type surface area measurements Carman & Raal (17) measured a pair of isotherms for weakly interacting systems; butane on silica, and ammonia on carbon black. They then permuted the adsorbents, for which case the adsorption is strong. The monolayer values

increased accordingly. It is clear from experiments of this type that the absolute measurement of surface area is not accomplished easily; it is none the less true that the nominal surface area assigned by measuring the nitrogen isotherm and using the BET method gives a surface area parameter of independent value and usefulness.

Another method of independently measuring a characteristic volume for a solid is provided by the measurement of dielectric constants of materials in the adsorped state. Waldman, Snelgrove & McIntosh (18) have reported measurements for ethyl chloride and butane adsorbed on rutile. The polar adsorbate exhibits a change in electrical properties over a small critical range of the volume adsorbed. This change seems to occur near the completion of a monolayer. No such sharp change is found with the butane.

Dacey & Thomas (19) have continued the study of the remarkable saran charcoal. Nitrogen isotherms and the heat of adsorption of nitrogen were determined. The heat declines monotonically from an initial heat of 4.6 kcal. The very large surface is thus understandably quite heterogeneous. Water adsorption shows no hysteresis, which indicates that pore-dimension is small. Large, bulky molecules, such as neopentane, are adsorbed slowly, while linear and planar molecules are adsorbed quickly. This fact and the planar structure of graphite suggest that the pores are plate-shaped: small in one dimension only.

The highly porous solids ("molecular sieves") chabazite and mordenite were modified by the preadsorption of polar sorbates by Barrer & Rees (20). The isotherms for a number of nonpolar gases were determined as a function of the amount of less volatile preadsorbed molecules which, at the temperatures of the isotherms, were essentially nonvolatile. The preadsorbed material sterically limited the penetration of the second species in a manner that corresponded to molecular bulk rather than the number of sites preoccupied. Also the large heat of adsorption of hydrogen on bare chabazite was progressively reduced as the mineral surface was covered by ammonia. Thus, the ammonia covers the more active portion of the surface first.

In a similar experiment, Singleton & Halsey (21) studied the adsorption of argon on preadsorbed layers of xenon on nonporous adsorbents. It was concluded that the xenon layers could only reach a finite thickness: less than two atomic layers on anatase and about six on graphitized carbon black. This was also shown to be true of krypton on carbon black (22). From a study of the solution of argon in the preadsorbed krypton layers, it was apparent that the film became unstable with respect to bulk crystallization at about six layers.

Briegleb & Scholze (23) made a thorough study of the mixed adsorption of chloroform and acetone on glass spheres. Unfortunately, they interpreted their data in terms of the meaningless Hüttig-Thiemer isotherm. The derivation of this modified BET isotherm violates the principle of microscopic reversibility [see, for example, Keii's paper (24)].

Theories of adsorption.—A variety of treatments of adsorption continue

to be based on the Langmuir equation, summed over a range of adsorption energies to yield an arbitrary isotherm. Treatments of this sort always involve one or more of a number of very restrictive assumptions that are easy to forget when actual data are being interpreted. Honig & Hill (25) have carefully discussed the following among them: (*a*) Adsorption occurs on a fixed number of sites. (*b*) The coverage is limited to a monolayer. (*c*) Each site is associated with a fixed adsorption energy. (*d*) No lateral interactions occur between adsorbed molecules. (*e*) Each adsorbed molecule is bound rigidly and does not move over the surface. (*f*) The distribution of adsorption energies is not altered during the adsorption process. (*g*) The partition function of the adsorbed molecule is independent of the adsorption energy.

All of these assumptions are involved in the typical evaluation of a distribution function for energy of adsorption. Even the more sophisticated method of extrapolating the heat of adsorption to absolute zero with heat capacity data, which Pace & Greene (26) have done for argon on rutile, is subject to all but (*g*).

It is well known that, for the particular case of an exponential distribution of Langmuir site energies, the Freundlich isotherm emerges if the summation (or, here, integration) is carried over all values of the energy, both positive and negative, to infinity. This has been interpreted by some to imply the existence of sites of repulsive energy in great quantity. Actually, since the sites in question would adsorb only a negligible quantity of material, the unrealistic limit is only a convenient artifact; now, Danon & Zamith (27) have demonstrated this point explicitly.

It is intuitively clear that the Langmuir configurational entropy

$$S_c = -R \ln (\theta/1 - \theta)$$

applies only if θ is the coverage on one kind of site and thus not to the total coverage if the surface is heterogeneous. It is, perhaps, not as clear that the expression does not apply if there is lateral interaction on a uniform surface, except as a zeroth approximation when the interactions are all small compared to kT. The use of this expression in the general interpretation of all isotherms by Graham (28) is thus semi-empirical.

De Boer (29) has continued his analysis of published isotherm data from the standpoint of the entropy of adsorption. He is able to make tentative distinctions between mobile and fixed-site adsorption on the basis of the value of the entropy and its variation with coverage. Steiner (30) has written down the general isotherm for a linear array of sites. This is of interest because it is the only isotherm including interaction that can be derived without any approximations.

Work on metal films.—In recent years, a number of papers have appeared which have clarified and amplified certain ideas and generalizations about the properties of evaporated metal films that were left in the air owing to the untimely death of Otto Beeck. The generalization that chemisorption on a clean metal surface is instantaneous has been investigated by Porter &

Tompkins (31). These authors studied the rate of adsorption of hydrogen and carbon monoxide on iron films prepared by careful degassing and evaporation of spectroscopically pure iron wire. The rate of adsorption was fitted to the equation

$$\ln r_S = \ln a - bq$$

where r_S is the rate of adsorption, a and b are constants, and q is the quantity adsorbed. This equation had previously been successfully applied to a very large amount of assorted data assembled by H. A. Taylor and the late N. Thon (32). No satisfactory unique derivation has been given for this equation, but it implies that whatever the mechanism, the activation free energy for adsorption increases linearly with the amount adsorbed. There is no saturation limit for the adsorption; it continues to increase at an exponentially decreasing rate. As Porter and Tompkins put it the essential significance of the adherence to this or any similar relationship for the rate is that "rate process is kinetically monotonic"; thus one cannot make Beeck's distinction between a fast initial uptake followed by a slow absorption into the interior.

In a second paper, Porter & Tompkins (33) study the rate of adsorption on iron films sintered at varying temperatures. In an attempt to compare their results with those of Beeck (on nickel) they made an arbitrary division between "slow" and "fast" at one minute of elapsed contact time with the gas. They do not find that the slow sorption is relatively independent of the degree of sintering and therefore of area. They, therefore, are not able to identify this slow sorption with a kind of solution, as Beeck did. They come, rather, to the reasonable conclusion that the effect of sintering is, first, to reduce the total surface for adsorption, and, second, to narrow the spectrum of adsorption energies on the surface. Note that this is essentially the same type of effect that heat treatment of carbon black produces with respect to that substance's behavior in physical adsorption of argon. One can only regret that this recent work is on iron, so that it is not possible to settle anything by comparing it with Beeck's generalizations about nickel.

In an interesting exploratory research, Trapnell (34) studied the adsorption of six gases on 20 metals, in the form of evaporated films. He was able to put the metals in groups and establish a hierarchy of gases with respect to their adsorption by these groups. Oxygen led the hierarchy, being adsorbed by almost all metals, while nitrogen was adsorbed by the fewest metals. There will no doubt be dissatisfaction voiced with some of Trapnell's assignments as nonadsorbers; however, on the basis of an admittedly arbitrary dividing line, he has presented an interesting summary of chemisorption on metal films.

The change in electrical resistance of a nickel film upon chemisorption has been studied by Suhrmann & Schulz (35). Adsorbates which, on the basis of ideas of chemical bond formation, would be expected to accept electrons from the surface increased the resistance, while those that would be expected to donate electrons decreased the resistance. Argon had no effect.

In a continuation of his earlier work, Kemball [see Anderson & Kemball (36)] has shown that

> evaporated metal films (11 metals) were able to catalyze the exchange reaction between ethane and deuterium at much lower temperatures than were required for the exchange of methane and deuterium. The metals which were active at the lowest temperatures (ca. −60°C.) produced monodeutero-ethanes as the main initial product and showed little tendency to form ethanes containing several deuterium atoms except by successive reaction. On the other hand with metals such as rhodium and palladium the main initial product was perdeutero-ethane, and this was attributed to a relatively high probability for an adsorbed ethyl radical to form an adsorbed ethylene molecule.

Although this explanation is couched in terms of an ethyl-radical mechanism, it is clear that the metals which produce highly deuterated products adsorb the ethane more tenaciously. This is certainly consistent with the fact that they are the higher-temperature group. Similar results were found for propane and isobutane (37). Rhodium caused multiple exchange, tungsten produced single exchange, and nickel was intermediate in behavior.

The work function.—In connection with a study of the theory of the field emission microscope, Gomer (38) has considered the effect of chemisorbed atoms on the work function of a metal. In contrast to the theory of the contact potential, a detailed examination of the geometry of the surface lattice is required. He considers individual dipoles to be arranged on the surface in triangular array, and then proceeds to discuss the work function at three locations on the surface so covered. He finds that this localized model for the surface layer leads to a work function increment much smaller than the contact potential. Essentially a new ad-atom can manage to go to a most favorable position on the surface, rather than, as Boudart suggested (39), enter a sort of electrical condenser with no periodic variations in the direction of motion parallel to the surface. The outcome is that Boudart's ingenious explanation of the fall in heat of chemisorption fails, on the basis of Gomer's more refined model, for two reasons. First, the fall in heat becomes convex to the coverage axis, rather than the linear (or even concave) experimental results, and second, the calculated fall in heat at half coverage becomes only about 8 kcal., for the case of oxygen on tungsten. This is only about a quarter of the experimentally observed value.

Using a model similar to Boudart's and using the ionization potential of the adsorbate molecule, Matsen, Makrides & Hackerman (40) have estimated the fraction of the surface that would be covered at saturation for a number of complex molecules on semiconductor and metal surfaces. The theory is in reasonable accord with experiment.

Para-hydrogen conversion.—The "physical" conversion of *para*-hydrogen to the equilibrium mixture over paramagnetic surfaces has been subjected to intensive study recently. Harrison & McDowell (41) used as catalyst $\alpha\alpha$-diphenyl-β-picryl hydrazyl, a solid free radical. The variation of the velocity constant with temperature was very small. Increase of temperature from 90° to 290°K. reduced the rate by a factor of about two. If the activa-

tion energy is negative it is customary to assume that the rate is lowered because the amount of physically adsorbed hydrogen ready to undergo reaction is reduced. [This energy of adsorption would be expected to exceed one kilocalorie (42)]. However, in this case, the energy is so slightly negative, a measurement of the adsorption isotherm was undertaken. It was shown that a small amount of hydrogen, corresponding to a few per cent coverage, was adsorbed at 90°K. Unfortunately, the data were not accurate enough to allow further analysis to be made. It is possible that the (negative) activation energy is so much smaller than the anticipated adsorption energy of hydrogen because of the existence of a compensating activation energy for reaction which, fortuitously, cancels most of the adsorption energy. However, the numerous cases where the activation energy is small make this *ad hoc* explanation rather unattractive.

Sandler (43) has investigated a number of catalysts in an exhaustive manner. The results on hemin are particularly detailed. The rate undergoes a fourfold decrease as the temperature is raised from 70° to 120°K. There it passes through a minimum, begins to rise steadily, until at 0° it reaches a maximum and stays roughly constant to the highest temperature reached (150°C.). *Ortho*-deuterium showed similar behavior below 150°K. Here it showed a maximum, but followed by another fall-off to a low rate at the highest temperature reached. The ratio of the two rates changed gradually in the region of the maxima, from near unity at low temperatures to seven at high temperatures.

These results are reasonably explained by a change-over in mechanism as the temperature is raised. At low temperatures the conversion takes place in a physically adsorbed film on sites which require little or no activation energy. As the temperature increases, sites requiring activation energy become active. The second decline in the deuterium rate requires that deuterium adhere to these sites more strongly than to the sites having no activation energy. The monotonic change in the ratio supports the dual mechanism. It is significant that the high-temperature ratio approaches the theoretical limits for gas-phase catalysis.

Results are also reported for two neodymium oxalate hydrate catalysts. Here the results are more fragmentary, but they still support the hypothesis of two competing mechanisms.

Sandler (44) has also studied the conversion over barium sulfate and titanium dioxide (rutile). The results on the latter are quite interesting. The surface was rendered oxygen deficient by long pumping (blue color). On this surface oxygen either depressed or increased the rate depending on both the quantity of oxygen and whether it was chemisorbed or not. A coating of D_2O suppressed reaction almost completely. Addition of oxygen then restored the rate.

In a following paper (45), the same author established that *ortho*-hydrogen is more strongly adsorbed than *para*-hydrogen, on the surface of rutile at 90°K. At this temperature, the separation factor is about 1.6.

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ELECTRODE PROCESSES AND THE ELECTRICAL DOUBLE LAYER[1]

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What follows is not primarily a résumé of the most recent papers in the field but a discussion of certain topics which have seemed to be of interest and within the writer's purview. In the selection of topics for discussion, an effort has been made to choose those which have not been previously reviewed in this series, or which have been touched upon only lightly. However, a certain number of topics have been reintroduced because the writer has felt disposed to say more about them or to treat them differently. Many other reviews of topics covered in this series are available (1 to 7), also a number of books (8 to 13), and an important collection of papers (14).

Most of the recent interest in electrode processes has been concernedwith the kinetics of those processes, whereas the interest in the electrical double layer has centered around its equilibrium properties. These topics can therefore be dealt with separately without too much overlapping.

Electrode Processes

The kinetics of electrode processes can be investigated experimentally by at least two superficially different modes of approach which we shall characterize as d.c. and a.c. methods, respectively. Under d.c. methods we shall include such variants as interrupted-current techniques and other methods which do not utilize the distinctive properties of sinusoidal alternating currents. Under a.c. methods we shall include only those procedures which utilize alternating currents for a study of the effects of electrode polarization, thereby excluding such topics as the conductivity of electrolytes and the measurement of dielectric constant. The more comprehensive view of a.c. methods has been reviewed recently by Gerischer (15) with respect to the techniques involved.

D.c. polarization studies.—The usual form of the Tafel equation for hydrogen overvoltage is mathematically improper in that it contains the logarithm of a dimensional quantity. A better form which also has the advantage of displaying the equation's kinetic significance is:

$$i = i_0 \exp(\alpha F\eta/RT)$$

where η is the overvoltage, i_0 is the current[2] which would flow at zero overvoltage if the equation were still valid there, and α is an empirical constant which generally, but not always (3), lies between 0 and 1. When α is less

[1] The literature survey pertaining to this review was concluded in November, 1954.

[2] It is also equal to the exchange current at zero overvoltage. It is assumed that concentration polarization is avoided by sufficient agitation.

than one, it is customary to call it the transfer coefficient and to interpret it as the fraction of the overvoltage (overpotential) acting to favor the charge transfer. The explanation generally given for the fact that the transfer coefficient is less than unity amounts to saying that the H atom is formed (i.e., the peak of the potential energy curve is reached) at a small but finite distance from the surface, where the potential energy of the H atom is greater than it is at the surface proper, to which it is then attracted with the degradation of the energy involved into heat. As the potential of the electrode is made more cathodic, the peak of the potential energy curve moves away from the surface slightly, so that one might regard the H atom as being formed in a state of greater potential energy. Thus, more of the available energy is dissipated as heat, making the process less efficient, and α less than unity. It is important to note that no actual electronic transfer is involved, since the electron is still in the metallic phase after the reaction. Thus, there is no precisely defined moment at which the H_3O^+ ion, together with its mirror image charge in the electrode, becomes an H atom and a water molecule. But it is convenient to think of the transition as occurring when the hydronium ion passes the potential energy peak, recognizing that this choice is natural but arbitrary.

It has been known for a long time that the value of α is diagnostic in the sense that values of α less than unity could only be accounted for in terms of a slow-discharge theory[3] of overvoltage (16). A second diagnostic criterion called the stoichiometric number, ν, was discussed in last year's review by Bockris [(17); also (9)] and in more detail by Parsons (17a, 17b). It has proved to be a difficult quantity to evaluate experimentally, and no new values have been published. Assuming that α is known and is less than unity, the present usefulness of the stoichiometric number lies in its capacity to distinguish whether the follow-up ("desorption") step in the cathodic evolution of hydrogen is the reaction $H+H \rightarrow H_2$ or $H+H_2O+e^- \rightarrow H_2+OH^-$. Except for mercury in alkaline solution (18), the rate-determining step on high-overvoltage metals, and probably for most others except Pt, Pd, Au, W, and Mo, appears to be the initial charge-transfer reaction (3). This conclusion had also been reached earlier (19, 20) for the cathodic evolution of hydrogen on mercury from neutral or acid solutions from the absence of a faradaic admittance (see below) corresponding to that reaction.

A different approach to the problem of proving the mechanism of electrode reactions is that of Vetter (21 to 24), and Gerischer (15, 25, 26, 27), who do not consider the hydrogen evolution reaction at all, but concern themselves with typical redox reactions not involving gases. It is of interest that the diagnostic methods of the English and German schools have never been experimentally applied to the same system.

The essence of the Vetter-Gerischer approach is twofold. In its first aspect the current is studied as a function of the potential, of the (controlled) rate

[3] By a slow-discharge theory we shall mean any theory in which the initial discharge step is rate determining.

of stirring, and of the concentrations of the various substances present in the solution. As the potential increases, there is always a limiting current at a particular rate of stirring, and this limiting current generally increases as the rate of stirring increases. In that case, the limiting current is diffusion controlled, and a study of the magnitude of the limiting current as a function of the concentrations of the molecular species present usually tells definitely what substance is limiting the rate of the reaction by its limited rate of diffusion to the electrode. If the limiting current is virtually independent of the rate of stirring, this fact indicates the presence of a slow precursor (*vorgelagerter*) reaction, one of whose products is needed for the electrochemical reaction. A study of the dependence of the limiting current upon the concentrations of the molecular species serves to identify, or at least to delimit, the substances involved in the slow precursor reaction. Finally, it can happen that the limiting current is decreased by stirring. This will occur when one of the products of the electrochemical reaction is needed for a slow precursor reaction.

Probably the best example of these diagnostic criteria is provided by the cathodic reduction of nitric acid in the presence of nitrous acid [Vetter (22, 28)]. The limiting rate increases not only with the nitric acid concentration, as expected, but also with the nitrous acid concentration. This suggests a rate-limiting precursor reaction involving both of these substances, or possibly substances with which they are in equilibrium. A reaction satisfying all requirements is that suggested by Vetter, viz:

$$HNO_3 + HNO_2 \rightarrow N_2O_4 + H_2O \qquad \text{rate determining at large current densities} \qquad 1.$$

Alternatively one might have:

$$NO_3^- + HNO_2 \rightarrow N_2O_4 + OH^-$$

Vetter suggests that the direct reduction of N_2O_4 is inherently much less probable than the direct reduction of NO_2[4] and therefore writes as a second not-rate-determining precursor reaction.

$$N_2O_4 \rightarrow 2\ NO_2 \qquad \text{fast} \qquad 2.$$

followed by the charge-transfer ("*Durchtritts-*") reaction

$$NO_2 + e^- \rightarrow NO_2^- \qquad \text{rate determining at low current densities.} \qquad 3.$$

This reaction is expected to be inherently fast, but it will, even so, be rate determining at the equilibrium potential, where the forward and backward

[4] The argument given is that a two-electron transfer is inherently much less probable than a one-electron transfer. This seems necessarily true on theoretical grounds whenever the electrons actually leave the metallic phase as a result of the reaction. Two-electron atomic transitions, for example, are unknown. On the other hand there are two-electron electrode processes (e.g., $Cd^{++} + 2\ e^- \rightarrow Cd$) in which the electrons never leave the metallic phase, and for these there is no theoretical need to postulate one-electron steps. So far as the writer is aware, this distinction has not heretofore been made.

rates are equal. At some slightly more cathodic potential the net forward rate of reaction 3 will approach the back-and-forth rate of reaction 1, the concentration of nitric acid will fall, and with a small further increase of potential, reaction 1 will become rate determining.

Since nitrous acid is a weak acid, reaction 3 will necessarily be followed by the rapid after-reaction (*angelagerter Reaktion*):

$$NO_2^- + H^+ \rightarrow HNO_2 \qquad \text{fast.} \qquad 4.$$

Since nitrous acid is needed for reaction 1, stirring lowers the concentration of an essential reactant, and the rate of the limiting reaction falls.

The mechanism thus indicated agrees also with the behavior of nitrous acid on anodic oxidation. Thus, a reasonable mechanism can be formulated and tested by the methods outlined. It is not usually possible to exclude all variants of a proposed scheme except by arguments of reasonableness, however.

The second aspect of the method of Vetter and Gerischer has to do with an interpretation of the rate of change of the potential with current (the polarizability) of an electrode at its equilibrium potential. When it is possible to hold all of the concentrations of the reactants constant while measuring this quantity (21, 26), $(dE/di)_o = RT/nFi_o$, where E is the potential, i is the observed current, and i_o is the exchange current at equilibrium. The subscript $_o$ on the differential coefficient implies that the measurement refers to a slope measured at the equilibrium potential. (This same meaning is sometimes denoted by the subscript $\eta \rightarrow 0$). The number of electrons involved in the charge-transfer reaction is n. The above equation is valid only when the charge-transfer reaction is rate determining, not only at the equilibrium potential (as it necessarily is), but also at those potentials where a just-measurable current flows. This could fail to be so in case the exchange current is large, when concentration polarization might prove unavoidable at attainable stirring rates (28a).

If the variation of the exchange current with concentration can be studied in this manner, the identity and coefficients of the reacting species in the exchange reaction (not necessarily the slow step in the ordinary sense) can be ascertained. It needs to be recognized that the chemical equation for the exchange reaction is not necessarily known *a priori*. Thus, Gerischer finds (29) that in the reduction of $Zn(NH_3)_4^{++}$ it is the species $Zn(NH_3)_2^{++}$ and $Zn(OH)_2$ (in solution) which are actually reduced. About eight such cases are now known (15, 30 to 33), together with a good many others which are no different from what one would expect (25, 34, 35).

Vetter (21) calls attention to the fact that the term "activation overvoltage" is ambiguous in cases like that cited above in which the activation energy of a precursor reaction is responsible for the limited rate of an electrochemical reaction. He suggests the term "reaction overvoltage" for such cases, and uses the term "*Durchtrittsüberspannung*" (charge-transfer overvoltage) for what is usually meant by activation overvoltage. In exactly the same way, the term "concentration polarization" is ambiguous, since the

lowered concentration of a substance required for the electrochemical reaction might arise either from its limited rate of diffusion to the interface or from its limited rate of formation from a precursor reaction.[5] To avoid this ambiguity, Vetter speaks of the diffusion polarization and the reaction polarization corresponding to the two possibilities cited.

In the above discussion, everything we have said about the substances needed for the electrochemical reaction can be applied in reverse to the substances formed from the reaction. Thus, a slow after-reaction can cause an accumulation of products and slow down the reaction by reaction polarization, the corresponding emf. being a reaction overvoltage.

It is also possible to distinguish heterogeneous from homogeneous rate-limiting reactions by studying the effect of poisons or surface-active coatings on an electrode [Vetter (22)].

The well-known polarographic technique has, in recent years, been investigated as a tool for the study of the kinetics of electrochemical reactions. This has been done by a detailed mathematical investigation of the effects of slow precursor reactions on reactions which are at least in part diffusion controlled. The concepts are similar to those described above for the Gerischer-Vetter method except that since no stirring is employed, the effects of diffusion are taken into account mathematically. The advantage of the method is that it permits the employment of a dropping mercury electrode, for instance; the disadvantage is that diffusion effects may seriously mask the kinetic effects under investigation. The subject has been thoroughly and well reviewed recently by Delahay (8).

The reduction of an ion takes place, not from the interior of the solution, but from the electrical double layer. Thus, the potential tending to assist or inhibit reduction is that between the interface and the outer Helmholtz plane (the plane of closest approach of a cation, called by Overbeek (2) the Gouy plane). Likewise, the concentration which should appear in the rate equation is not the concentration in the interior of the solution, but that at the outer Helmholtz (Gouy) plane. These facts and others are discussed by Frumkin (36) in a comparison of certain American theories of hydrogen overvoltage (36a to 36e) with his own.

It is apparently believed by some authors that the effect of the electrical double layer on the rate of an electrochemical reaction is insignificant or perhaps completely accounted for by the introduction of a thermodynamic activity coefficient, but this is demonstrably incorrect. Thus, a tenfold increase of the ionic strength[6] at constant hydrogen ion concentration will

[5] In the latter case the required substance will be brought to the surface by diffusion also, to be sure, but Vetter considers that this is the less important source of the substance.

[6] To be more nearly correct, it is not the ionic strength which is determining but the concentration and charge of the cations present in solution. The anions play a role, too, not primarily by virtue of their charge and abundance, but rather by virtue of their chemical properties.

generally decrease the concentration of the hydrogen ion in the double layer roughly tenfold, whereas its effect on the thermodynamic activity coefficient will, under the same circumstances, ordinarily be small. Moreover, it is not at all certain that the thermodynamic activity coefficient has any significance at all in hydrogen ion discharge rates even at constant ionic strength. Those factors which make for low activity coefficients (bridge ions) are mostly the same as those which catalyze the hydrogen ion discharge reaction. As a result of these considerations, it is not very meaningful to discuss hydrogen overvoltage as a function of hydrogen ion activity (or pH), although this is very often done. These facts are also implicit in the paper by Frumkin cited above (36).

The role of the electrical double layer in the reduction of anions (especially $S_2O_8^{--}$) has been investigated in a series of papers by Kryukova (37), Nikolaeva *et al.* (39, 40), Frumkin *et al.* (38, 39). At low ionic strengths there is a falling off of the current as the cathode goes from a state of positive to a state of negative charge. This result arises from the sudden lowering of the concentration of anions in the double layer as the sign of its charge reverses. The effect is recommended as a means of determining the potential of zero charge on solid metals [Kalish & Frumkin (41)]. Foreign cations suppress the effect in a manner comparable to their effect on the stability of negatively charged lyophobic colloids, and for essentially the same reason, namely, that they tend to annul the potential of the outer Helmholtz (Gouy) plane of the double layer. The effects of adsorbed anions and of hydrogen ions upon the reduction of $S_2O_8^{--}$ have been studied by Kalish & Frumkin (41).

Bagotskaya & Frumkin (42) have investigated anew what has sometimes been called the transmission of hydrogen overvoltage through an iron membrane, on one side of which hydrogen is being evolved cathodically while the potential is measured relative to an acid solution on the other side. Hydrogen diffuses through the membrane as hydrogen atoms during the measurements, and the amount so diffusing has also been measured. The idea underlying this experiment is that if the slow step in the cathodic evolution of hydrogen on iron is the combination of hydrogen atoms to molecules, then there must be an equilibrium between hydrogen atoms and hydronium ions in solution. Then the potential of the metal relative to the solution should depend upon the concentration of hydrogen atoms on the surface of the metal, and this should reveal itself when electrolysis is begun on the other side of the membrane. A positive effect of this sort was observed by Fischer & Heiling (43), whereas Bagotskaya & Frumkin observed no effect. It can be argued that leaks in or around the membrane will produce positive effects, whereas there is no obvious way in which a positive effect could be missed if there really is such an effect. This follows particularly in an experiment where the quantity of diffused hydrogen is measured, as in the new experiments cited. The transmission of hydrogen overvoltage through a palladium foil was demonstrated in 1944 by Frumkin & Aladjalova (43a) and constitutes direct proof that the combination of hydrogen atoms on palladium is not a fast reaction.

The "cause" of hydrogen overvoltage is still occasionally discussed. Most workers in the field would agree that this discussion springs from a misconception of the overvoltage concept. When the power supply to a working electrode is suddenly interrupted, the potential does not instantaneously return to the equilibrium value for a number of reasons, chief among which is the fact that the electrical double layer acts as a charged condenser which holds the potential and continues the electrochemical reaction at a rate which is the same, at the first moment after current interruption, as it was before the interruption. There is no mysterious source of potential to be accounted for. At the moment of interruption a measurement of the rate of change of the potential gives a measure of the capacity of the electrical double layer according to the equation $C_{dl} = -i/(dE/dt)$. (This equation has been used by Hansen & Clampitt (44) to infer the extent of the adsorption of surface-active materials on solid metals.) The mathematical details of the time-rate of decay of potential after current interruption have been analyzed by Frumkin (20), by Grahame (45), and in greater mathematical detail by Scott (46). It is concluded in the latter two papers that the interpretation of decay curves can give no more information about the kinetics of an electrode process than is given by bridge measurements. Those quantities which are determined most easily by one method are also those which are obtained most easily in the other.

Piontelli and his collaborators have for a number of years been concerned with the problems of measuring overvoltages of metallic ion deposition on metals (47). They avoid the uncertainties of the commutator or current-interrupter method by using a modification of the classical Luggin capillary, which they have brought to a state of high accuracy for the conditions prevailing in their experiments through a study of scaled models and other factors (48, 49). In the electrodeposition of metals from aqueous solutions a very serious difficulty arises from the tendency of metal deposits to "tree" or else to deposit in unstable forms (i.e., under strain), In either case, the measurement of ion-deposition overvoltages is rendered difficult and inaccurate. There is an added difficulty in that charge-transfer (activation) overvoltage is so small that concentration polarization effects predominate. Piontelli and his group (50) have recently succeeded in building workable cells for the measurement of overvoltages in molten metal/salt systems, thus overcoming both of the above-named difficulties. They find (51) that the cathodic overvoltage in the system molten $Pb/PbCl_2$ at 520°C. is very low (not over a few mv.) over a wide range of current densities extending up to 2 A/cm.^{2} Work is reported under way for similar systems involving tin and indium.

The commutator or current-interrupter method of measuring overvoltage and double layer capacity has been brought to a high state of electronic perfection by Schuldiner & White (52) and by Yeager *et al.* (53, 54), In the investigations of both of these groups, potential measurements of good accuracy could be made within 10^{-6} sec. of the current interruption. The apparatus has been used by Schuldiner to measure the capacity of the double

layer[7] and the overvoltage of hydrogen on bright platinum (58), including a study of pH and salt effects. Yeager *et al.* (54, 59, 60) have used the technique for a study of the effect of ultrasonic waves on hydrogen overvoltage on the electrodeposition of copper (61), and for a study of the cathodic polarization of the oxygen electrode on carbon surfaces in alkaline solutions (62). According to these authors, the cathodic reduction of adsorbed oxygen to $HO_2^- + OH^-$ [a process which requires two electrons going from the electrode to the solution and which should therefore be regarded as requiring two one-electron steps; cf. (6, 9, 62a)] is under these conditions a fast and reversible reaction. They suggest that this is so chiefly because the O—O bond is not broken in the reaction. As evidence in support of this suggestion they cite an observation of Weisz & Jaffe (63) which indicates that the reaction

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad 5.$$

is much faster than the reaction

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O. \qquad 6.$$

Iofa (61a) supposes that reaction 5 goes by way of O_2^-, HO_2, and HO_2^- as intermediates. Hacobian (62a), on the other hand, cites reasons for believing that the adsorbed oxygen is first dissociated into atoms and then reduced in the presence of water to $OH + OH^-$. Two OH radicals then combine to form H_2O_2.

It is known (62a, 63, 64, 65) that oxygen is more or less reversibly reduced to H_2O_2 in alkaline solutions on mercury also. The reaction is catalyzed by the plumbite ion (66), and in the presence of this catalyst the reaction can be detected by its effect upon the impedance of the electrode, as explained below, even in reasonably well deaerated solutions. The reaction thus constitutes a sensitive test for dissolved oxygen, and has the important advantage of being highly selective.

The oxygen-hydrogen peroxide equilibrium at a mercury electrode has also been studied by Yablokova & Bagotski (65) who were able to show for the first time that the electrode potential varies in the proper manner with changes in the concentration of oxygen as well as with the other substances involved in the equilibrium. Their results lead to a new and considerably different value for the standard free energy of hydrogen peroxide in solution ($\Delta F = -32{,}900 \pm 100$ cal.). Earlier results of Berl (64) are essentially confirmed.

The mechanism of the reduction of oxalic acid at a mercury electrode has been investigated by Florianovich & Frumkin (67). They find that the primary act of electroreduction is the electron transfer to the molecule in question, hydrogen playing no part. The ion $HC_2O_4^-$ also fails to react because at the potentials in question it is repelled from the electrode by the

[7] Robertson (55) and Kheifets & Krasikov (98) and, earlier, Dolin & Ershler (57) have also measured the capacity of the electrical double layer on bright platinum using a.c. methods. The results are discussed in a later section.

electronic charge on the mercury surface (cf. reaction of $S_2O_8^=$ cited above).

A discussion of adsorbed films (of organic substances on electrodes) and of their relation to electrical discharge processes taking place through them has been given by Frumkin (68), who asserts as a general principle that the rate of an electrode process in the absence of an adsorbed layer is determined by the rate of the electrochemical reaction itself, and not by the rate at which a hypothetical reactant (for example atomic hydrogen) is produced at the electrode. From the discussion of the reduction of nitric acid given above, it would seem that this statement of the proposition is a little too broad. It should probably be limited to the assertion that reductions on high-overvoltage metals do not occur via a hydrogen atom stage.

Frumkin goes on to state that the presence of an adsorbed layer produces a reduction in the rate of an electrochemical reaction involving ion transfer through it partly because of the influence of the adsorbed layer upon the potential of the outer Helmholtz (Gouy) plane and partly because the presence of the adsorbed layer necessitates the partial or complete dehydration of the reacting species prior to the ion transfer through it. It is not a question of a low rate of diffusion of the ion through the adsorbed layer, but rather of a low rate of the ion's entering the layer.

A.c. polarization studies.—From an instrumental point of view, the impedance of an interface is probably its most accurately measurable property. Attempts to interpret the measured property in the presence of a reversibly reducible substance began with Wien in 1896 (69) and have continued with increasing success to the present day. The work of Ershler (70, 71, 72), Randles (73), and Gerischer (74, 75) are representative of the modern point of view. The work has been interpreted and the basic postulates re-examined by Grahame (76). A clear and condensed summary has been given by Delahay (77). The main concepts are as follows: The resistance of the solution is in series with the impedance of the interface and can be subtracted out of the measured impedance. What remains is the impedance of the interface.[8] This impedance is made up of two parallel impedances (or admittances, which is the more significant concept when elements in parallel are under consideration), one being the admittance of the electrical double layer, the other being the admittance of the electrode resulting from any faradaic processes which involves an appreciable exchange current.[9] It is not necessary that the forward and reverse components of the current be equal, although the mathematical treatment is simplest when they are. There is only a slight

[8] The impedance of the other electrode, which is also in series, can generally be made negligible by a judicious choice of electrode shapes and sizes.

[9] A faradaic process which is accompanied by a negligible reverse current, $\overleftarrow{i}$, will give rise to no faradaic admittance. That is why hydrogen ions and small amounts of oxygen do not prevent a mercury electrode from behaving as an ideal polarized electrode as far as its impedance is concerned. That is also why it is possible to conclude from the absence of a faradaic admittance on mercury in the presence of hydrogen ions that the reverse current is always small, so that the discharge process is never reversible.

and presumably negligible interaction between the two kinds of admittance, for which reason they can be treated independently. In the absence of a slow precursor or slow *angelagerten* reaction, it can be rigorously proved. (71, 73, 74, 76) that the faradaic admittance can be represented by a new kind of "equivalent circuit" as follows:

In this circuit θ is a pure resistance in the sense that it does not change magnitude with frequency and does produce an emf. in phase with the faradaic current. θ is a measure of the intrinsic speed of the reaction and is simply related to the exchange current at equilibrium, i_o, through the relation $\theta = RT/nFi_o$ (cf. with equation for polarizability cited above) where n is the number of electrons involved in the faradaic process. In the above circuit —W— has been called by the writer the "Warburg impedance." It is not representable at all frequencies, even at a single potential, by ordinary resistors, condensers, and inductors, but can be represented at any one frequency and potential by a series or parallel combination of a resistor and a condenser. Expressed as a series combination, the impedances of the two elements are equal at any one frequency, giving rise to a 45° phase shift, and vary inversely as the square root of the frequency. These properties have been confirmed and used to evaluate the exchange current on mercury surfaces by Randles & Somerton (73, 78), Gerischer (29), Vetter (32), and Rosenthal & Ershler (72). On solid metals the experimental problem is more difficult, but necessary to solve if one wishes to study the many problems involving redox systems which are reversible at potentials where mercury is oxidized. A certain amount of success has already been achieved (78, 79).

Randles & Somerton (78) have measured the exchange current as a function of temperature and thus obtain the heat of formation of the activated state. This quantity is found to be much smaller than the energy of hydration of the ion, and also smaller than the energy of interaction of a metal atom with the amalgam into which it moves. Thus, the activated state is one in which the influence of the solvent on the ion is still practically undiminished, and the influence of the amalgam on the newly formed atom of metal is also nearly as strong as that of the atom dissolved in mercury. As will be shown in the next paragraph, the activated state appears to involve a "bridge" atom or molecule as well.

Randles & Somerton (78) have also studied the influence of anions upon the exchange current of the systems Eu^{++}/Eu^{+++}, Zn/Zn^{++}, and Bi/Bi^{III} and find that those anions which are specifically adsorbed on mercury have a large positive catalytic effect on the exchange current, thus bringing into consideration the bridge theory of homogeneous electron exchange advanced by Libby (80) and in slightly different form by Taube & Myers (81) and Taube & King (82). In the Libby theory it is emphasized first that electron

exchange must take place according to the Franck-Condon principle, according to which the nuclei do not move during the transfer of the electron. In order for the potential energy of the activated state to be low enough for electron transfer to occur, a bridging atom or molecule is considered necessary, because then the activated state will not be under excessive strain from too abnormal a distribution of solvent molecules after the electron transfer. It is not clear how this argument applies to electrode exchange reactions, however, for which a bridge atom nevertheless seems to be necessary. In any case, the Franck-Condon principle does not apply to reactions such as $Zn^{++}+2e \rightarrow Zn$ where the electron never leaves the metallic phase. Libby also emphasizes the need for symmetry of the electron-exchanging partners. Although the results of Randles & Somerton (78) confirm the need for a bridge, they do not otherwise meet the specifications for exchange enunciated by Libby. Taube & Myers (81) think that the function of the bridge atom (or molecule) is to hold the reacting partners together, thus giving the electron transfer (or ion transfer in cases such as $Zn^{++}+2e \rightarrow Zn$) more time in which to happen. Water proves to be a poor bridge for electron-transfer reactions; polarizable anions are much better, as had been indicated earlier by Piontelli (83), and as might have been inferred from polarographic experience, where the addition of chloride ion often steepens the current rise.

A very surprising feature of Randles & Somerton's results is the observation that the accelerating influence of chloride ion on the Eu^{++}/Eu^{+++} exchange at a mercury electrode is found at potentials so cathodic that the bridging anion is practically not at all adsorbed on the mercury, this latter being fairly certainly known from other lines of evidence (84). Apparently, the chloride ion forms a complex with either the europous or europic ion in solution (rather than with the metallic mercury), and it is this complex which then undergoes oxidation or reduction when it touches the electrode. Very likely the mercury retains the chloride ion temporarily as a by-product of the electron transfer. Meier & Garner (85) have studied the homogeneous europous-europic ion interchange and find that it, too, is catalyzed by chloride ion. The mechanism is almost surely the same. They attribute the result to a mono-chloro complex with the europic ion, but it seems evident from their data that it is more likely the europous ion which is complexed.[10]

Taube & King (82) offer evidence suggesting that a chloride ion may in some cases catalyze an electron exchange without actually serving as a bridge. This is particularly significant in its relation to the influence of anions on electrode reactions which do not involve actual electron transfer (i.e., the reduction of cations to the metal).

[10] This follows from their observation that in the presence of chloride ion the europous ion does not reduce water rapidly, showing that the activated state involving the europous ion is chemically altered by the presence of the chloride ion. The same conclusion follows less directly but almost as certainly from other evidence cited by Meier and Garner, tending to prove that the europic ion is not in itself complexed. It is highly unusual for the lower of two valence states of an ion to be the more readily complexed, but this appears to be a valid example of such a situation.

Rosenthal & Ershler (72) have made a study of the Hg/Hg_2^{++} exchange, and obtain considerable experimental verification of Ershler's theory of a.c. polarization described above. These authors have also investigated by the same method the chemisorption of chloride and oxide (or hydroxide) ions on mercury at the large positive potentials where equilibrium with these ions prevails. This work serves to bridge the gap between ordinary chemisorption of anions, where chemical reaction as such is not considered to take place at the electrode, and the reversible electrochemical process by which potentials are established in galvanic cells. There is no sharp line of demarcation between these two states, as Rosenthal & Ershler's work makes clear.

Hillson (79) has succeeded in measuring the exchange current with cupric ions at a solid metallic copper electrode. The method of removing surface-active impurities with chromatographic alumina is new to this work and appears to be effective. Hillson concludes that the exchange reaction is rapid, but that it occurs almost exclusively at active centers (unlike mercury) and that the effect of adding small amounts of surface-active substances is to cover the inactive parts of the surface preferentially.

Gerischer (29) has used the a.c. impedance of an electrode to measure the exchange current as a function of the concentrations of the substances which could be participating in the charge-transfer reaction. This procedure gives the coefficients of the charge-transfer reaction (not of the inherently slowest step). The results are used in the same way as was described above under d.c. polarization methods; indeed the a.c. impedance method may be regarded simply as a better way of measuring the polarizability of an electrode. It is better because concentration polarization is very much less with a.c. than with d.c. and also because the coefficient dE/di is measured directly as a resistance rather than indirectly as a slope of a curve. At the same time it has been possible by a.c. impedance methods to determine accurate values of α, the transfer coefficient, for a variety of electrode reactions (29). These do not generally lie close to $\frac{1}{2}$. The values obtained by independent investigators are found to agree very satisfactorily (29, 78).

The Electrical Double Layer

If, in the impedance measurements mentioned in the last section, one takes care not to have any reversibly reducible or oxidizable substance present, what is measured is the differential capacity of the electrical double layer. The first successful application of this type of measurement was that of Proskurnin & Frumkin in 1935 (86). A variant of the method was developed by the present writer (87) and applied to the measurement of the capacity of the double layer between mercury and aqueous solutions of simple electrolytes (88 to 94). It is necessary for success in these measurements to produce a clean smooth surface with all of the elements of the surface exposed to the same conditions of current flow (88). The use of a dropping mercury electrode or stationary mercury droplet is an effective way of satisfying these requirements. The impedance is almost always measured

with a bridge, other methods having invariably proved less accurate. With minor modifications this is also the scheme used by Gerischer (29), Randles (73, 78, 95); Rosenthal & Ershler (72); and Melik-Gaikazyan (96). The results of the latter on the capacity of 1 *N* KCl have been compared with unpublished results obtained by the writer and found to be in very good agreement.

For many years it has been a somewhat unsettled question whether or not the electrical double layer comes to equilibrium "instantaneously," i.e., in a time short compared to the period of the alternating current used for its measurement. Until 1946 all measurements of the capacity of the double layer showed some dispersion (change with frequency) suggesting a delay in the establishment of equilibrium. In that year it was shown (88) that the dispersion on mercury could be almost completely eliminated by taking sufficient care to avoid "shading" of the merucury droplet by the glass wall of the capillary. These results have now been confirmed and greatly extended by Melik-Gaikazyan (96). Some dispersion remains when surface-active organic molecules are present, but Frumkin & Melik-Gaikayzan (97) have shown that this dispersion arises from the finite rate of diffusion of the molecules to the surface and not from any measurable delay in their adsorption.

It is frequently stated that the rate of adsorption of Cl^- on platinum was shown by Ershler to be slower than on mercury. A careful reading of Ershler's papers (70, 72), however, will show that this was not his conclusion. What he did conclude was that chloride ion inhibits the adsorption of oxide ions, meaning that it inhibits the formation of a surface oxide of the metal. There is no evidence yet available to show that the adsorption of chloride ion on the surface of any metal is slow.

The influence of surface-active substances on the hydrogen overvoltage and differential capacity of a platinum electrode have been measured in a new work by Kheifets & Krasikov (98), who study these properties as a function of the potential. They obtain results quite similar to those obtained earlier by other investigators using mercury. In particular, the differential capacity goes through a minimum in the presence of caprylic acid, for instance, and shows two desorption peaks, one on either side of the minimum. Sodium caprylate shows only on desorption peak (on the cathodic side of the minimum), corresponding to the fact that a capillary-active anion cannot usually, if ever, be expelled from an anodic surface by the influence of the field on the dipoles of the solvent. It is of interest that total desorption of surface-active substances was never obtained with platinum, this being in marked contrast to their behavior with mercury. The authors attribute this difference to the inhomogeneity of the solid surface.

The differential capacity measured by an impedance bridge is related to the electronic charge q on the surface by the equation $C = dq/dE$. Integration of CdE then gives Δq. According to the Lippmann equation $d\sigma/dE = -q$, where σ is the interfacial tension. Therefore, integration of qdE gives the

electrocapillary curve except for a constant of integration. These well-known facts are cited to show that the differential capacity is a thermodynamic function which is as significant as the interfacial tension for the calculation of thermodynamic properties of metal-solution interfaces, and which can often be measured with higher precision. Two constants of integration must be obtained in other ways, however, (84) and this is often a major limitation to the usefulness of capacity measurements for calculations based on the thermodynamic theory.

A recent comprehensive presentation and critique of the thermodynamic theory of electrocapillarity is that of Parsons (1). All authorities are now in agreement as to the major points of the theory, although several widely different ways of looking at the problem have their advocates. The application of the thermodynamic theory of the double layer has made it possible to evaluate the individual ionic components of charge in the electrical double layer from differential capacity measurements (84).[11] Although it is not thermodynamically necessary to do so, it is often expedient to use the Guoy-Stern theory (1, 89) of the diffuse double layer to evaluate certain constants of integration. It is found (84) that monatomic cations are not adsorbed on mercury, except by simple electrostatic attraction in the diffuse double layer, [but see Devanathan (100) who thinks cations undergo a special kind of adsorption described below] whereas anions are adsorbed on positively charged mercury almost without exception. This adsorption is over and above the electrostatic adsorption expected for the diffuse part of the double layer. Such adsorption is called specific adsorption and is greater (for anions) on positively charged than on uncharged or negatively charged mercury. Thus, one has the unique possibility of continuously varying the strength of a chemical bond by continuously varying an electrical potential.

Among anions, the fluoride ion alone shows no easily detected specific adsorption on positively charged mercury (84). The other halogens show increasingly great adsorption in the expected order. In general, the adsorption of anions on positively charged mercury parallels the solubility of the corresponding mercurous salts (93). It is not known whether the adsorption of anions on other metals parallels the solubility of the corresponding metallic salts, or whether the order is one fixed by the properties (e.g., the polarizability) of the anions alone.

From a knowledge of the components of the charge in the electrical double layer it has been possible (84) to compute the potential of the outer Helmholtz (Gouy) plane with no significant theoretical uncertainty unless Devanathan's theory (100) discussed below is correct. This has long been regarded as one of the objectives of electrocapillary and electrokinetic measurements.

[11] It has always been possible to do this from interfacial tension measurements, but the accuracy needed is uncomfortably high. Nevertheless, this has been done in a number of cases, most recently by Devanathan & Peries (99). The thermodynamic theory underlying the determination of individual ionic components of charge runs parallel to that which permits the determination of individual ionic transference numbers from measurements of the electromotive force of galvanic cells.

It is also possible to compute the amounts of specifically adsorbed and nonspecifically adsorbed anions separately.

Because of the nonadsorption of fluoride ion, solutions of soluble fluorides are particularly suitable for studies of the "ideal" properties of the electrical double layer. It has been shown by Grahame (94) that the differential capacity of dilute aqueous solutions of sodium fluoride can be rather accurately predicted from those of a more concentrated solution by assuming that the capacity of the region between the metallic surface and the plane of closest approach of the cations (the outer Helmholtz or Gouy plane) is a function of the surface charge density q only.

The shape of a single differential capacity curve gives significant clues as to the adsorption or nonadsorption of the individual ions of the electrolyte to which it corresponds. Thus, if two differential capacity curves are found to be alike, it is virtually assured that the specific adsorption of their corresponding ions (i.e., the anion of one compared to the anion of the other, etc.) will be alike. This conclusion follows thermodynamically if the curves are alike at all concentrations, since the variation of the capacity with concentration is thermodynamically related to the individual values of the ionic concentration (84). Devanathan (100) has recently formulated a theory which would permit the calculation of the concentrations in the electrical double layer of anions and cations separately from a single differential capacity curve (rather than from two or more, as can be done thermodynamically). In this theory the minimum on the capacity curves, which can be observed with solutions of all electrolytes, is interpreted as a point of no specific adsorption. The rise in the capacity which occurs on either side of this minimum is then attributed to a specific adsorption of cations or of anions, as the case may be. Specifically adsorbed cations are supposed to lie in the inner Helmholtz plane, essentially the same, except for its exact position, as that in which anions are held on anodic polarization. It needs to be understood, however, that by the term "specific adsorption," especially as applied to cations, Devanathan does not mean what other authors have commonly meant by that term.[12] He means a nonspecific holding of the partially desolvated cations in an inner plane by electrostatic forces of an otherwise unspecified nature. The capacity of the regions between the mercury surface and the inner Helmholtz plane, and between the latter and the outer Helmholtz (Gouy) plane, are assumed independent of potential. This very novel feature of the theory is adopted as a first approximation to the truth and not because it is regarded as inherently very probable. The numerical results are in reasonably good agreement with experiment (99). However, it needs to be recognized that the numerical successes achieved in the original paper (100), and in a sequel by Devanathan & Peries (99), may not, in fact, depend upon the new postulates of the theory in any very significant manner. This matter awaits further analysis.

[12] The author is grateful to Dr. Devanathan for private correspondence leading to a clarification of this point.

Macdonald (101) has attempted to deduce the capacity of the nondiffuse part of the electrical double layer, in the absence of specific adsorption, from a consideration of the combined effects of dielectric saturation and compression of the solvent by the electrostatic field. Owing to the presence of several constants which need to be evaluated from the experimental data, it is not possible to say definitely whether or not the theory succeeds in its aims. The values found for these constants are physically reasonable, however, which is all that one can expect at present. The theory contains the first mathematical treatment of the idea that the rise in the differential capacity of the double layer which is observed on strong cathodic polarization is attributable to the compression of the solvent by the electric field. A major defect in the theory is that it predicts symmetrical behavior of the capacity of the electrical double layer around the potential of zero charge, whereas this is never observed in fact.

Parsons & Devanathan (56) have made a detailed study of the electrocapillary curves of Hg in contact with solutions containing HCl dissolved in methanol-water mixtures covering the range from pure water to pure methanol. Sufficient data were obtained to permit evaluation of those quantities which are thermodynamically defined for such systems in 0.01 N HCl. It was observed that methanol is progressively "squeezed out" of the interface and replaced by the more polar water molecule as the cathodic polarization increases, a result in harmony with the much more abrupt squeezing out of larger molecules such as octyl alcohol under similar circumstances (86, 88). The authors also observe what they interpret as specific adsorption of chloride ions on a negatively charged mercury surface. An alternative possible interpretation of their observations is that undissociated HCl molecules are so adsorbed. In either case the marked effect of chloride ions upon the hydrogen overvoltage of mercury is accounted for, since the chloride ions undoubtedly serve as a bridge for the electron transfer, as stated above.

Over a period of years the Russian school of workers has exhibited interest in a phenomenon which we may call the Esin & Markov effect, after its discoverers (102). This effect has to do with the observation that the potential of the electrocapillary maximum on mercury varies with the concentration of a surface-active anion such as iodide ion at a rate which sometimes exceeds a theoretical upper limit of 2.303 RT/F per tenfold change of activity of the surface-active anion. [The theory of this upper limit has been discussed recently by Parsons (1) and by the writer (103).] The effect is attributed by Esin & Markov (who credit the idea to Frumkin) to the fact that in the Stern theory, including its more recent modifications [see (1)], the forces of interaction between the adsorbed ions parallel to the interface are neglected. Then, as a result of the mutual repulsion of such ions, they will tend to arrange themselves in a regular hexagonal lattice, much distorted by thermal agitation, to be sure. The work required to move an ion into such a lattice is much less than that calculated for an immobile smeared-out charge of the same magnitude because the ions already present make

room for the incoming ion by separating and thus keeping at a distance from the incoming ion. A mathematical formulation of this theory has been given by Esin & Shikov (104) and revised by Ershler (105). Their treatment has been supplemented by a suggestion (103) to the effect that the chemical bond lying between the mercury and the adsorbed anion is almost surely in itself a source of an oriented dipole (apart from the dipole arising from the known charge separation, an effect which is absent at the potential of the electrocapillary maximum), and that this oriented dipole could well account for the Esin & Markov effect in whole or in part. The suggested new dipole thus bears the same relation to the known separation of charge at potentials other than that of the electrocapillary maximum as does the dipole moment of a covalently bonded molecule to that of a completely ionized salt molecule. Therefore, the situation is that the Esin & Markov effect has been explained twice over, and it remains to be determined which explanation relates to the major part of the effect. Ershler claims that his theory accounts quantitatively for the whole of it (105).

The differential capacity of smooth ("bright") platinum has been studied as a function of potential by Schuldiner (58), Robertson (55), Kheifets & Krasikov (98), and Dolin & Ershler (57, 106). Not much similarity between the results of the various investigators is to be observed. There are so many experimental difficulties to be overcome in this measurement that it is impossible to tell which, if any, of the results are to be trusted. Dolin, Ershler & Frumkin (106) used their results to ascertain the rate of the charge-transfer reaction in the discharge of hydrogen, this having been the first really serious attempt to use the theory of the faradaic admittance mentioned in the previous section. Their final conclusions still seem reasonable, even though their measurements must be held to be of doubtful accuracy because they were made at a time when the necessity for smoothness and spherical symmetry (or any other symmetry which assures an equal flow of current to all parts of the electrode surface) was not sufficiently appreciated. Robertson (55) points out the enormous increase in the apparent series resistance which is observed with platinum electrodes as the frequency is lowered, an effect also noted by the writer (66) not only with platinum but also with other types of solid electrodes and to a lesser degree even with mercury. The effect with mercury has been observed and apparently explained by Rosenthal & Ershler (72) as being due to the creeping of the solution up the inner walls of the capillary from which the mercury issues. It is not clear that any similar explanation will suffice to explain the results observed with solid microelectrodes. The (series) capacity of a spherically symmetrical smooth solid electrode is virtually unaffected by the frequency of the measuring signal in the absence of a faradaic admittance (55, 66). This fact can be used as a test for smoothness and symmetry of an electrode.

The capacity of solid Ni (106a, 106b) and solid Cu (106c) electrodes in acid and alkaline solutions has been investigated recently. Although the copper electrodes were not spherically symmetrical or especially smooth, their series capacity was reported to be independent of frequency, in striking

contrast with the experience of most other investigators.

Borisova, Ershler & Frumkin (107, 108) have devised a method of measuring the capacity of the electrical double layer at the surface of solid metals which can be melted at moderate temperatures (Tl, Cd, and Pb). The method employs a pendant droplet formed from the melt and so arranged that the surface does not shrink as the liquid solidifies. This is necessary to avoid crinkled surfaces. The range of voltages over which the electrode is sufficiently polarizable is not very great, but suffices to show the general similarity of the capacity curves so obtained to those commonly obtained with mercury. At low concentrations the differential capacity goes through a sharp minimum which marks the potential of the electrocapillary maximum. The latter potential is shifted by an amount roughly equal to the difference in the work functions of the metals compared [cf. ref. (1)]. This implies that orientation of solvent molecules and potential differences arising from the distribution of electrons on the uncharged surface are not very different for the various metals studied, so that the apparent potential differences are just contact potential differences occurring outside the cell.

Renewed interest has arisen in connection with what is now called the Billiter potential. This is a new name for the apparent potential of what used to be called a "null" electrode. The latter is prepared by finding a surface-active electrolyte such that the reversible potential of a given metal immersed in it is also the potential of the electrocapillary maximum, i.e., the potential of zero electronic surface charge. An old and discredited idea was that such an electrode was without potential difference. Nevertheless, the potential of such electrodes retains a surprising constancy as measured against a fixed reference electrode and uncorrected for contact potentials outside the cell [Oel & Strehlow (109)]. An explanation for this constancy has been offered by Delahay (110) based on the idea that the work function of the metal cancels out that of the observed potential because an electron must in effect traverse the interface twice, once in each direction, in the circuit employed in the measurement.

A method of measuring the capacity of the electrical double layer which does not involve an electrode at all has been devised by Overbeek (2, 112) and Mackor (111). The surface on which the measurements have been made is the surface of a colloidal suspension of silver iodide. The potential difference between the AgI particles and the solution could be controlled by the addition of very small amounts of silver ion or iodide ion in excess, the potential difference being governed formally by the Nernst equation. The charge on the colloidal particles is measured by the uptake of the potential-controlling ions from the solution. This makes it possible to represent q as a function of E (in the presence of an excess of an inert electrolyte), and hence dq/dE, which is the differential capacity. The striking feature of the results is their similarity to those obtained with mercury. In both cases there is a moderately strong increase of capacity on the anodic or positive side of the potential of zero charge and a relatively low capacity on the cathodic or negative side. In both cases the effect of the low capacity of the

diffuse double layer in dilute solutions near the point of zero charge is realized also.

The kinetic theory of the diffuse double layer, originated by Gouy and Chapman, was incorporated in the theory of Stern. The dielectric constant of the solvent is assumed constant in spite of the large electric fields known certainly to be present, and the question arises whether or not this fact invalidates the theory. In order to answer this question one needs to know first how the dielectric constant (which should now be called the differential dielectric coefficient) varies with field strength. Grahame (114, 115) has devised a semiempirical equation which happens to agree almost perfectly with a fully theoretical functional dependence given by Booth (113). It is a straightforward but somewhat tedious task to compute the properties of the diffuse double layer from this equation, and Grahame conclude (114) that although the differential dielectric coefficient almost certainly falls to low values in the diffuse part of the double layer, the measurable properties of the double layer are not significantly affected. Experiment tends to bear out this conclusion (94).

Conway, Bockris & Ammar have also investigated this problem (116) but start with a very different assumed functional dependence of dielectric coefficient upon field strength. In spite of this difference, these authors arrive at numerical results not very different from those of Grahame. They choose to interpret their results differently, however, stressing the disagreement with classical theory. As mentioned above, this disagreement is perhaps more apparent than significant.

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POLYMERIZATION KINETICS AND POLYMER PROPERTIES[1]

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Introduction

Except for a section on copolymerization (1), previous reviews in this series have not discussed the kinetics of polymerization. It is fitting to treat this subject at this time, since there have been published in 1953 and 1954 books dealing entirely or in part with polymerization kinetics by Burnett (2), Flory (3), Weissberger & Friess (4), and pertinent review articles by Burnett & Melville (5), and Pepper (6). Earlier comprehensive sources include books by Küchler (7) and Alfrey, Bohrer & Mark (8), and review articles by Burnett (9) and Mayo & Walling (10).

Part one of the present review deals with the kinetics of addition polymerization, and Part two with those aspects of the physical chemistry of polymer solutions relating to properties determined by the mechanism of polymerization.

KINETICS AND MECHANISM OF ADDITION POLYMERIZATION

Free Radical Mechanisms

Initiation.—The usual sources of free radicals for the initiation of addition polymerization include organic peroxides and azo compounds. The decomposition rate constants for several peroxide initiators were studied by Swain, Clarke & Stockmayer (11). Lewis & Matheson (12) and Bawn & Mellish (13) obtained similar data for azo compounds. The use of a radioactive initiator provides a means for determining the rate at which initiator fragments become incorporated into the polymer. If the rate of decomposition of the initiator is known independently, it is possible to calculate the efficiency with which initiator radicals induce polymerization. Arnett (14, 14a) and Bevington and co-workers (15, 16), using C^{14}-labeled α,α'-azo-bis-isobutyronitrile, found efficiencies slightly greater than 50 per cent for the polymerization and copolymerization of several monomers. Walling (17) compared the rate of decomposition of diphenylpicrylhydrazyl by radicals from azoisobutyronitrile with the rate of catalyst decomposition and calculated a somewhat higher efficiency of 70 per cent.

[1] The survey of the literature pertaining to this review was concluded in January, 1955.

The initiation of polymerization by highly intense radiation fields was reviewed by Ballantine (18). This method offers advantages of controlled polymerization at low temperatures, in the absence of foreign substances such as initiators, or in the solid state. Dainton (19) used γ- and x-rays to initiate the polymerization of acrylonitrile in aqueous solution by means of hydrogen and hydroxyl radicals. γ-rays from radium were used by Chapiro (20) to initiate the polymerization of various monomers alone and in solvents which are dissociated into radicals by the γ-rays. β-rays from radioactive strontium or from Van de Graaf generators were used with various monomers by Schmitz & Lawton (21) and by Seitzer, Goeckermann & Tobolsky (22). Mund and co-workers (23) used α-rays from radon to initiate the gas phase polymerization of vinyl chloride. Slow neutrons were used by Landler & Magat (24) to initiate several monomers by radicals generated in the neutron-induced decomposition of ethyl bromide or by the capture of γ- and β-rays from that decomposition.

Various dyes were used as sensitizers for photopolymerizations. Dyes were used alone in pure monomer by Bamford & Dewar (25) and Melville & Whyte (26); in the presence of benzoyl peroxide by Ueberreiter (27); and with reducing agents in aqueous solutions by Oster (28).

Propagation and termination.—The propagation step in free radical polymerization consists merely in the attack of a free radical upon the monomer double bond. There seems to be no controversy with regard to this step. Except for a few cases, termination of the growing radical chains proceeds by mutual deactivation of two free radicals either through combination or through disproportionation, i.e., the transfer of an atom between the radicals giving one saturated and one unsaturated molecule. Conclusive evidence as to which of these two possibilities predominates in specific cases was recently obtained for the first time by Bevington, Melville & Taylor (16, 29). Styrene and methyl methacrylate were polymerized with C^{14}-labeled α,α'-azo-bis-isobutyronitrile. The numbers of initiator fragments per molecule were determined by measuring the molecular weights of the polymers by osmometry and the specific radioactivity of the polymers and the initiator. At 25° and 60°C., polystyrene terminates by combination. At 0°C., methyl methacrylate terminates by disproportionation about 1.5 times as often as by combination; at 25°, about twice as often; and at 60°, about six times as often. The energy of activation for disproportionation is greater than that for combination by about 4 kcal. per mole.

Absolute rate constants.—In order to measure separately the rate constants for the propagation and termination steps in radical polymerization, it is necessary to measure the lifetime of the growing polymer chain. This has usually been done by the use of the rotating sector technique (2, 5) in which the rate of a photopolymerization is measured under constant and intermittent illumination. This method integrates over a large number of the individual induction and decay periods during which the rate of polymerization builds up when the illumination begins and decays when it is interrupted. Several newer methods measure directly the natural induction period be-

tween the commencement of initiation and the attainment of the steady-state reaction rate. Precision dilatometry was found useful by Burnett (30) in systems with long radical lifetimes; a precision of one part of polymer in 10^7 was achieved. A group of methods was developed by Melville and coworkers (31 to 34) in which the heat of polymerization was measured in an adiabatic system by one of several means: If the temperature rise was measured directly by a thermocouple (31), a resolution in time of 0.1 second and in temperature of 2×10^{-4}°C. was achieved. The half-life of heat loss in the vessel (in air) was 720 sec. The method was useful in following reaction to high conversions. If the temperature rise was measured by the change in refractive index of the system, using a Jamin interferometer (32), a resolution of 0.02 second and 1×10^{-4}°C. was achieved with a heat half-life of 180 sec. If the temperature rise was measured by following the change in dielectric constant (33, 34), a resolution of 10^{-4} sec. and 10^{-5}°C. was achieved with a half-life of 60 sec. Other methods include that described by Bamford & Dewar (35), based on the increase in viscosity of the polymerizing medium while illuminated intermittently, and that described by Goldfinger & Heffelfinger (36) and Hicks & Melville (37) in which free radicals are generated and terminated at different points in a flowing system.

Extensive compilations were made by Burnett & Melville (5, 38) of experimental values of the individual rate constants. A few typical values are presented in Table I. Sets of values for the same monomer from different investigators may show large discrepancies.

TABLE I

ABSOLUTE RATE CONSTANTS FOR CHAIN PROPAGATION AND TERMINATION AT 30°C.*

Monomer	k_p	$k_t\times10^{-7}$
Styrene	55	2.5
Methyl metacrylate	143	0.61
Vinyl acetate	1240	3.1
Methyl acrylate	720	0.22

* After Flory (3).

Chain transfer.—The mechanism of chain transfer involves a radical-molecule reaction in which a growing chain radical is terminated and the molecule involved (called the transfer agent) becomes a free radical capable of adding monomer units. A prominent mechanism of chain transfer is the removal by a chain radical of a hydrogen or halogen atom from a molecule. Mayo, Gregg & Matheson (39) showed that in a polymerization of undiluted monomer, transfer may take place with monomer or initiator molecules. Transfer to monomer occurs independent of reaction rate whereas transfer to initiator increases rapidly with increasing rate, since high rates involve high initiator concentrations. Baysal & Tobolsky (40) found that transfer to

hydroperoxide initiators takes place much more readily than that to peroxide or azo initiators.

The most widely studied transfer reactions are those taking place with solvent molecules. Extensive compilations of the transfer constants for such reactions were made by Burnett & Melville (5, 38). A few typical values are presented in Table II. The relative efficiency of various substances as chain

TABLE II

CHAIN TRANSFER CONSTANTS FOR VARIOUS SOLVENTS AND RADICALS AT 80°C.*

Solvent	$k_{tr}/k_p \times 10^4$ for		
	Styrene	Methyl Methacrylate	Vinyl Acetate
Benzene	0.059	0.075	
Cyclohexane	0.066	0.10	
Toluene	0.31	0.52	92.
Ethyl benzene	1.08	1.35	
Carbon tetrachloride	130.	2.39	
Tetrachloroethane	18.	0.20	10,000.

* After Flory (3).

transfer agents varies widely with molecular structure. Aromatic hydrocarbons are rather unreactive unless they have benzylic hydrogens. Aliphatic hydrocarbons become more reactive when substituted with halogens. Carbon tetrachloride and tetrabromide are quite reactive. The reactivity of various polymer radicals to transfer varies widely; transfer reactions offer a valuable means for comparing radical reactivities.

Chain transfer to polymer is important in the production of branched polymer chains (see discussion of branching, below).

A chain transfer reaction in which the resulting radical is resonance stabilized to the extent that it cannot add monomer is termed a degradative chain transfer. This phenomenon, which may also be called autoinhibition, was found to occur in the polymerization of allyl acetate by Bartlett & Altschul (41), and in the polymerization of vinyl benzoate by Burnett & Wright (42).

Inhibition and retardation.—Inhibitors and retarders react with chain radicals to form products incapable of adding monomer. The difference between the two is considered to be one of degree rather than kind. Inhibitors may be free radicals, such as diphenylpicrylhydrazyl [Bartlett & Kwart (43)] or molecules such as quinone or benzoquinone [Schulz (44); Foord (45)] which produce radicals too stable to initiate polymerization. Walling (17) suggested that true inhibitors may be used to determine the rate of formation of free radicals in a polymerizing system (see discussion of initiation above). The use of inhibitors in this way is to be viewed with suspicion, how-

ever, since it is often found that one inhibitor molecule stops more or less than one radical. If, for example, the radicals generated by the reaction of an inhibitor molecule with a chain radical are themselves destroyed by disproportionating with each other, one inhibitor molecule stops two chains. In contrast to the above reaction of benzoquinone in catalyzed styrene polymerization which was studied by Cohen (46), Mayo & Gregg (47) found that many quinone molecules are used up for each chain radical generated in the thermal polymerization of styrene. Schulz & Kämmerer (48) found that benzoquinone can also undergo transfer with styrene chain radicals, reducing molecular weight but not rate. The triphenylmethyl radical was shown by Mayo & Gregg (47) to initiate chains as well as inhibit them (the latter much more efficiently). The following classification was suggested by Flory (3) for substances which modify the course of polymerization reactions: (*a*) If free radicals themselves, they can either initiate or inhibit polymerization, or both. (*b*) If they are molecules reacting to generate radicals, these radicals can (*i*) be completely unreactive, in which case the substance is an inhibitor; (*ii*) add monomer, in which case the substance is a comonomer; (*iii*) undergo transfer, in which case the substance is a chain transfer agent.

In any of these cases the polymerization may be retarded rather than inhibited if the subsequent reactions are slow.

Copolymerization.—The kinetics of copolymerization have been discussed in an earlier review in this series (1). There it was shown that the initial composition of a copolymer could be calculated from the composition of the monomer feed and values of the monomer reactivity ratios r_1, r_2, which are the ratios of the rate constant for a given radical adding its own monomer to that for its adding the other monomer. A nomograph was published by Whelan (49) to facilitate this calculation.

If the above analysis is correct, only the last monomer unit added to the growing chain radical influences the relative ease with which the two monomers can then add to the radical; all units farther back in the chain can have no influence. Barb (50) has found recent evidence, however, that the penultimate monomer unit does have some influence on the subsequent addition of monomer. Merz, Alfrey & Goldfinger (51) showed that in this case four reactivity ratios corresponding to the four possible types of radicals must be considered. The effect is particularly pronounced with monomers of the type CHX=CHX, where X is a dipole. It has been detected in copolymers of styrene with maleic anhydride and fumaronitrile.

There are three possible termination reactions among the two types of growing chains in a simple copolymerization. Several additional parameters appearing when these are considered in the kinetics were defined by Melville, Noble & Watson (52). These are $\delta = k_t^{1/2}/k_p$ for each monomer and a cross termination frequency factor ϕ. In all cases studied so far (16, 53 to 59), values of ϕ indicate that cross termination is the favored reaction. The value of δ in copolymerization with a solvent present was recently found by Bradburn & Melville (60) to depend upon solvent concentration, whereas ϕ and the reactivity ratios did not. Several explanations were advanced

for this sensitivity of radical-radical interactions to environmental effects, but a choice among them cannot yet be made.

Several cases were found in which normally unreactive molecules act as comonomers. Stockmayer & Peebles (61) investigated the copolymerization of benzene with vinyl acetate during chain transfer experiments. Kice (62) studied wastage of inhibitor by copolymerization in the polymerization of methyl methacrylate.

Graft and block copolymers.—There has been considerable interest in preparing copolymers which, unlike ordinary copolymers, have long sequences of one monomer followed by or attached to long sequences of the second monomer. Especially in cases where the two homopolymers have quite different properties, the properties of the graft or block copolymers should be unique.

Graft copolymers made by polymerizing vinyl acetate in the presence of a styrene-vinylidene chloride copolymer were discussed by Mark (63). Some of the vinyl acetate radicals abstracted chlorine atoms from the polymer chain, after which vinyl acetate branches were produced. (Some vinyl acetate homopolymer was formed; this was separated from the graft copolymer by solubility difference.) This graft copolymer had a hydrophobic backbone and hydrophilic branches. The reverse situation was obtained by polymerizing styrene in the presence of a maleic anhydride-vinyl trichloroacetate copolymer. Variations of this process were used by Schmets & Smets (64) and Hayes (65).

Block copolymers have been synthesized in several ways: (*a*) Dunn, Stead & Melville (66) made polystyrene with bromo- and tribromomethyl end groups, by polymerizing styrene in the presence of CBr_4. The polymer was dissolved in methyl methacrylate monomer and irradiated with ultraviolet light. This produced free radicals by the photochemical removal of bromine atoms from the polymer. A block copolymer of styrene and methyl methacrylate resulted. (*b*) Dunn & Melville (67) suspended droplets of styrene in an aqueous solution of methacrylic acid. The polymerization was initiated in the aqueous phase. Some of the polymer radicals diffused into the styrene droplets, where polymerization continued. (*c*) Polymer radicals were generated in monomer in a capillary tube by intense ultraviolet radiation by Hicks & Melville (37, 68) and by Goldfinger & Heffelfinger (36). The monomer flowed continuously through the capillary and into a large vessel filled with the second monomer. By making the flow time from initiation to the point of discharge into the second monomer less than the radical lifetime, a block copolymer resulted. In these cases very little of either homopolymer was formed. (*d*) Photolysis of polyvinyl ketone in the presence of acrylonitrile was used by Guillet & Norrish (69) to produce free radicals and a block copolymer. (*e*) Styrene was polymerized by Smets & Woodward (70) with phthalyl peroxide under mild enough conditions that only one of the peroxide groups on a catalyst molecule was decomposed. Later this polymer was heated more vigorously with methyl methacrylate monomer to form a block copolymer.

Branching.—The special case of chain transfer to polymer with subsequent growth of a new chain on the polymer radical results in branched polymer. If an appreciable amount of this branching occurs, very large molecules containing many branches can be built up. Branches produced solely by transfer to polymer cannot build up infinite networks (since a new end is produced for each branch point). However, networks can be formed from these large molecules by a relatively few crosslinks.

Wheeler (71) described the possible transfer reactions to both monomer and polymer for vinyl acetate. He showed that the maximum molecular weight and degree of branching increase with conversion and can be expressed in terms of kinetic rate constants. Bevington, Guzman & Melville (72) studied branching by polymerizing nonradioactive monomer in the presence of radioactive polyvinyl acetate. They concluded that the polyvinyl acetate radical abstracts hydrogen from a polymer molecule at a rate comparable to that for hydrogen abstraction from small molecules. Similar radiochemical studies (73) showed that branching is of little importance in polystyrene as ordinarily prepared.

Wall & Brown (74) used α-deuterostyrene to reduce branching by the isotope effect (deuterium transfers about one-fifth as fast as hydrogen at 70°C.). They also concluded that ordinary polystyrene is essentially unbranched. Rugg and co-workers (75) measured total branching in polyethylene by infrared analysis of end groups. Cotman (76) studied branching in polyvinyl chloride by converting the polymer to a hydrocarbon and measuring the total number of end groups by infrared. Hayes (77) obtained the transfer constant for polybutadiene by a graft polymerization study.

Roedel and co-workers (78) demonstrated two kinds of branching in polyethylene: long-chain branches formed as a result of transfer to "dead" polymer molecules, and short-chain branches formed as a result of "backbiting" or transfer a few carbon atoms back along the growing chain. Bryant & Voter (79) treated the infrared spectrum of polyethylene in terms of short-chain branches since Billmeyer (80) and Beasley (81) showed that the number of long-chain branches is small compared to the total number of branches.

Theoretical analysis of the kinetics of branching and its effects on molecular weight distribution were made by Fox & Gratch (82), Bamford & Tompa (83), and Beasley (81). In general, the molecular weight distribution curve is broadened; i.e., the ratio of the weight average to the number average increases with the degree of branching.

Branches may also be produced by polymerization through the double bond of previously formed polymer, as in polybutadiene, or copolymer, as styrene-butadiene copolymer, though this reaction is usually referred to as "crosslinking." Morton (84) studied these reactions in the emulsion polymerization of dienes. Drysdale & Marvel (85) studied crosslinking in the emulsion polymerization of butadiene; they found that branching by chain transfer to polymer is not important in this system. Smets (86) produced branched polymethyl methacrylate by copolymerization with small quan-

tities of ethylidene dimethacrylate. Simpson and co-workers (87) studied the structure of branched (crosslinked) polymers of diallyl phthalate.

The Ionic Mechanisms

In addition to the free radical mechanism described above, polymerization can also take place through both carbonium ion (cationic) and carbanion (anionic) mechanisms. In comparison to free radical studies, these ionic polymerization mechanisms (88) have received relatively little attention. Pepper (6) has published a critical review of much of the available literature on ionic polymerizations. Another good source of material on cationic polymerization is a book edited by Plesch (89) which consists principally of twenty-five papers presented at a conference held at the College of North Staffordshire in 1952. These papers provide "progress-reports" by active investigators in the field, omitting experimental data, much of which is published in journals.

Characteristics of ionic polymerization which have hindered a thorough investigation include (*a*) very rapid polymerization rates at low temperatures (as low as −100°C.) so that a steady state and reproducible rates are difficult to establish; (*b*) the heterogeneous system usually produced by inorganic catalysts and organic monomers; and (*c*) the abnormally large effects produced by a third component (cocatalyst) when present in very small concentration.

Cationic polymerization.—Metal halides are usually employed as catalysts for cationic polymerization; those most commonly used are $AlCl_3$, BF_3, $AlBr_3$, $TiCl_4$, and $SnCl_4$. All of these are strong electron acceptors. Monomers which respond best to cationic polymerization contain groups which promote the release of electrons at the double bond. Such monomers, which can form high molecular weight polymers only by cationic mechanism, include isobutylene, isoamylene, vinyl alkyl ethers, α-methyl styrene, and *p*-isopropenyltoluene. Some monomers can be polymerized by either carbonium ions or free radicals: styrene, butadiene, divinyl ethers, methyl vinyl ketones, and N-vinyl pyrrolidone. Cationic polymerization is not effective on monomers which contain strong electron attracting groups; examples include the vinyl halides, vinylidene halides, vinyl esters, acrylic esters, and methacrylic esters.

Plesch (90), in a discussion of the theory of cationic polymerization, stated that in every system which has been rigorously investigated the polymerization of olefins by metal halides depends upon the presence of some third substance, the cocatalyst. The cocatalyst may be water, an alcohol, or an organic acid. Its function is to combine with the metallic halide into an ionogenic complex to provide the ions which start the polymerization proper. In media of low dielectric constant (such as a hydrocarbon solvent) the positive and negative ions must remain close together as an ion pair throughout the polymerization. In solvents of high dielectric constant, the ions may separate and form distinct kinetic entities. After the addition of each monomer unit, the cation is regenerated throughout the polymerization process.

The mechanism of termination is by no means clear, but it must involve rearrangement of an ionic complex, sometimes with and sometimes without the consumption of the catalyst. Transfer to monomer and solvent molecules may also take place.

Recent publications include a discussion of a physicochemical theory of the polymerization and copolymerization of isobutylene by Blouri (91). Eley & Saunders (92) studied the kinetics of the polymerization of *n*-butyl vinyl ether catalyzed by I_2, ICl, and IBr, and the inhibitory effects of pyridine and 2-iodopyridine. Overberger & Endres (93) reported the relative rates of attack of carbonium ion pairs on aromatic compounds in solution. Richardson (94) made an infrared study of polybutadienes and polyisoprenes prepared with Friedel-Crafts catalysts. Linear structures corresponding to 1,4, 1,2, and 3,4 addition are present in about the same ratios as in free radical polymerization but account for only about 50 to 75 per cent of the total material.

Anionic polymerization.—The anionic (carbanion) mechanism has been studied even less than the cationic mechanism. In general, the anionic mechanism is believed to be similar to the cationic mechanism except that negative ions catalyze the polymerization instead of positive ions. Monomers containing strongly electronegative groups can be polymerized in the presence of reagents capable of generating carbanions. Beaman (95) showed that sodium in liquid ammonia is particularly effective. Methacrylonitrile readily polymerized to high molecular weight in such a solution at −75°C. Grignard reagents and triphenylmethyl sodium were also effective catalysts; Foster (96) and Beaman (95) found that acrylonitrile and methyl methacrylate could also be polymerized. Butadiene and isoprene were found by Robertson & Marion (97) to polymerize at moderate rates in the presence of metallic sodium at ordinary temperatures. Sanderson & Hauser (98) and Higginson & Wooding (99) found that styrene can be polymerized to low molecular weight by the NH_2^- ion in a solution of potassium amide in liquid ammonia.

Ionic copolymerization.—Copolymerizations by cationic or anionic mechanisms tend to be more discriminating than those propagated by free radicals.

TABLE III

COPOLYMERS FORMED FROM A 1:1 STYRENE-METHYL METHACRYLATE FEED (8)

Catalyst	Temp., °C.	Type of Polymerization	Per Cent Styrene in Initial Polymer
Benzoyl Peroxide	60	Free Radical	51
Light	60	Free Radical	51
None	130	Free Radical	51
$SnCl_4$	30	Carbonium Ion	99
BF_3 Etherate	30	Carbonium Ion	99
Na	30	Carbanion	1
K	30	Carbanion	1

Often relatively pure polymer is obtained by ionic polymerization of monomer mixtures, whereas copolymer is readily obtained by free radical polymerization in the same system. Table III illustrates this. Determination of reactivity ratios for monomers has been restricted to a few examples (2, 3, 100). Little tendency for monomer alternation was found in ionic polymerizations, in contrast to the results found for free radicals. Overberger and co-workers (101) reported the effect of different Lewis acid catalysts on monomer reactivity ratios. Rehner and co-workers (102) derived equations for ionic copolymerization in an open system, one in which new catalyst is introduced as a dilute solution; the results were applied to the low temperature copolymerization of styrene and butadiene.

Miscellaneous Studies

A special type of ionic polymerization, the formation of polymethylene from the decomposition of diazomethane (CH_2N_2) with the evolution of nitrogen, has been studied by Bawn & Rhodes (103). Copper stearate and BF_3 were used as catalysts. An ionic mechanism was proposed which satisfies the observed kinetics; the rate of polymerization is first-order with respect to both catalyst and diazomethane. Teltzin, Restaino & Mesrobian (104) extended this work to the polymerization of diazoethane, diazobutane, and mixtures of diazomethane and diazoethane.

Alfin polymerization apparently involves a surface reaction. It refers to the polymerization of butadiene or other dienes by means of a specific combination of allyl sodium, $CH_2{=}CHCH_2{}^-Na^+$, a sodium alkoxide such as sodium isopropoxide, and an alkali halide, such as sodium chloride. This reagent, known as an alfin catalyst, produces polybutadiene of very high molecular weight at very rapid rates at room temperature. Morton (105) summarized the work on this catalyst and the resultant polybutadiene; details of the work appear elsewhere (106 to 109).

Mesrobian and co-workers (110) studied the solid-state polymerization of acrylamide initiated by γ-rays from cobalt 60. Polymerization occurred readily at 35° and 55°C. although the monomer shows little or no tendency to polymerize below its melting point in the absence of radiation. There was a long induction period at 5°C., but apparently free radicals were formed and trapped at this temperature because the material polymerized rapidly upon being warmed to room temperature. Henglein & Schulz (111) also studied this process.

Small (112) measured the vapor pressure of methyl methacrylate monomer in equilibrium with its polymer over the temperature range 100 to 160°C. He obtained good agreement with the equilibrium pressure of monomer calculated from the propagation and depolymerization rate constants.

Crosslinking by Radiation

There has been much recent interest in the crosslinking and degradation of polymers by high energy radiation, such as γ-rays from an atomic pile, and by high-energy electrons. Charlesby (113 to 116) announced the effects of

γ-rays on polyethylene in an atomic pile. The radiation causes cleavage of C—H bonds with the subsequent formation of gaseous hydrogen and crosslinking of the polymer chains by recombination of radicals. An increase in the total unsaturation of the polyethylene was observed together with other changes in minor structural features. Changes in the physical properties of the polymer were also studied. Crosslinking produced by radiation enabled the polymer to hold its shape above its crystalline melting point. Very large doses transformed polyethylene into a rubbery material and then into a glass-like solid.

Charlesby (117, 118) also studied the degradation of polymers to lower molecular weights by pile radiation. Both crosslinking and degradation reactions attracted the attention of other workers (119 to 124). Ballantine (18) summarized much of the work in this field. Miller and co-workers (125) studied the effect of chemical structure of vinyl polymers on crosslinking and degradation. In general, the polymers which crosslink have at least one α hydrogen atom on the monomer unit (—CH_2CH_2— or —CH_2CHR—); those polymers which do not contain α hydrogens (—$CH_2CR_1R_2$—) degrade; the chains rupture rather than crosslink. An exception to this general rule is polyvinylchloride which degrades (120).

A special application of radiation crosslinking has been in the determination of molecular weight and molecular weight distribution. The crosslinking reaction should be a truly random one and the relative rate of crosslinking should be proportional to the molecular weight of the various polymer molecules. Consequently, the larger ones should become insoluble first. Measurements of the gel content versus radiation dose give information about the molecular weight distribution; measurement of the molecular weight of the sol fraction gives additional information. Charlesby (126 to 129) presented a theoretical and experimental treatment of this method. He also derived equations describing changes in the molecular weight distribution when the polymer degrades rather than crosslinks (118).

Baskett (130, 131) has presented an alternative and more complete treatment of the problem of measuring the molecular weight distribution by radiation crosslinking. His experimental results for the original molecular weight distribution of polyethylene agreed well with theoretical predictions based on chain branching by free radical transfer during polymerization (see above).

POLYMER PROPERTIES IN SOLUTION

The properties of polymers in solution have been extensively treated in previous reviews of this series (132, 133, 134) from an essentially physical point of view. In this section, recent investigations on solution properties are considered, except for brief excursions, from the more limited standpoint of their contributions to questions of mechanism. More general accounts are found in the books of Flory (3) and Stuart (135).

Number-average molecular weight; osmotic pressure.—Since number-average molecular weights are most simply and directly related to the fea-

tures of a polymerization mechanism, their accurate determination is highly desirable, but unfortunately it is, in general, still very difficult. Cryoscopic and ebullioscopic methods are capable of considerable accuracy, as shown in the recent work of Schulz & Marzolph (136) and of Schön & Schulz (137), but they are restricted to quite low molecular weights (say below 40,000) and require stringent removal of low molecular weight contaminants. The experimental difficulties of osmotic pressure measurements, which were reviewed at some length by Wall & Hiller (134), were discussed by Broatch & Greenwood (138). Anomalous concentration dependence was reported by Grassie & Vance (139). New types of membrane for osmometry were described by Immergut and co-workers (140), those made of polychlorotrifluoroethylene being especially promising because of their chemical inertness and resistance to high temperature. Stabin & Immergut (141) developed an improved Zimm-Myerson osmometer with better membrane support which allows more rapid attainment of equilibrium and thus may reduce the uncertainties (142) in correcting for diffusion of solute through the membrane. This is particularly important for the unfractionated polymers that must be investigated in mechanism studies.

Light scattering.—The principles and practice of light scattering were reviewed by Sadron (143). Conventionally, weight-average molecular weights are obtained by extrapolation of the reciprocal reduced intensity of scattering to zero concentration and angle, usually by the method of Zimm (144). For very polydisperse systems of very high molecular weight this extrapolation may become difficult, and Benoit, Holtzer & Doty (145) suggested that in such cases more meaningful results can be obtained from the asymptotic behavior of the reciprocal scattering function $P^{-1}(\theta)$ at large angles. The intercept at zero angle of the asymptotic line, as Benoit (146) showed, gives the number-average molecular weight, but only for strictly linear Gaussian chains. The method was applied to cellulose nitrates (147). However, for more flexible macromolecules up to molecular weights of a few million, the conventional method still seems preferable, particularly if Zimm's procedure for obtaining the limiting tangent to $P^{-1}(\theta)$ is fully exploited, as in a recent study of polyvinylacetate by Shultz (148).

The controversy about absolute turbidities of pure liquids or other standard scatterers has continued. Maron & Lou (149, 150), Trap & Hermans (151) and Sedláček (152) report new calibrations which confirm the high values first found by Carr & Zimm (153); but Zimm's suggestion (154) that necessary refractivity corrections were omitted from the older work which gave lower values was rejected by Rousset & Lochet (155) and Guinand & Tonnelat (156). However, this still seems to be the most likely reason for the discrepancy. Although the question is, of course, a purely experimental one, appeals to theory have intruded. Thus, Maron & Lou (150) showed that their turbidity values for four pure liquids are in excellent agreement with the familiar Einstein-Smoluchowski equation. On the other hand, theoretical criticisms (157) of Einstein's derivation have been recalled (156, 158) in support of the lower turbidity figures. It is, therefore, worth

reporting that Fixman (159) showed that Einstein's result follows from a rigorous molecular theory. It is also clear from the work of Halwer, Nutting & Brice (160) and of Cantow & Schulz (161) that the higher calibration must be used in the usual Debye equation to obtain the correct molecular weights of solutes.

New designs of light-scattering apparatus were described (161 to 166). The turbidity of water, sometimes useful in assessing stray light contributions, was redetermined (167, 168).

It has been known for some time that branching has considerable influence on the scattering function $P(\theta)$, and qualitative indications of branching have been obtained in this way (169, 170). Theoretically, however, it was found (146, 171) that the influence of branching is largely counteracted by that of the great polydispersity inherently present in branched polymers. A quantitative assay of branching from light scattering alone is therefore scarcely possible at present, but is more easily achieved by a combination of light scattering with viscosity measurements (see below).

A novel light-scattering experiment, described by Wippler & Benoit (172), consists of measuring the change in scattering caused by a strong electrostatic field applied to the solution at several different angles to the direction of the incident beam. The field tends to orient the particles, changes the phase relationships among the scattering elements, and thus alters the scattered intensity by an amount initially proportional to the square of the field strength. The effect is greatest for highly polar polymers with rigid chains; it has been observed with cellulose nitrate, and also with rigid colloidal particles (173, 174). Since the magnitude of the effect depends strongly on molecular weight, it offers in principle a means of studying polydispersity, but for the majority of flexible macromolecules it is probably too small to be useful for this purpose.

Viscosity.—In spite of the need for calibration by an absolute method, it seems certain that viscometry, because of its simplicity and speed, will continue to be the kineticist's favorite method of determining molecular weights. Hermans (175) reviewed experimental and theoretical knowledge of viscosity and other hydrodynamic properties of polymer solutions in several chapters of a recent book.

Cragg, Sones, & Dumitru (176) recommended that poor solvents be generally employed for viscometric determinations of molecular weight, if possible at the Flory temperature Θ (3), which is the maximum temperature of liquid-liquid phase separation for a polymer of infinite molecular weight and also the temperature at which the osmotic second virial coefficient vanishes. The advantages of such a solvent are: (*a*) shear effects are appreciably smaller than in good solvents (177); (*b*) the constant a in the familiar equation

$$[\eta] = KM^a$$

for the limiting viscosity number is known (3) to be $\frac{1}{2}$ in such solvents, and hence need not be treated as an unknown parameter in the calibration; and (*c*) the concentration-dependence is less than in good solvents, thus facili-

tating the extrapolation to infinite dilution. These are considered to outweigh the disadvantages of (*a*) lower magnitudes of $[\eta]$ and hence somewhat lower precision; (*b*) more restricted choice of solvents; and (*c*) possibility of association effects. To the above recommendation may be added a second one, that light scattering be preferred to osmotic pressure for the calibration of the viscosity law. This is not only because the experimental difficulties of the former seem smaller at present, but also because viscosity-average and weight-average molecular weights are so close to each other (even for $a = \frac{1}{2}$) that little or no fractionation is necessary, while the osmotic calibration requires highly fractionated samples. The calibration may also be performed by means of sedimentation and diffusion measurements, as in the recent studies of polyvinylalcohol by Dieu (178) and polyacrylamide by Scholtan (179). Crystalline polymers below their melting points present a special problem, for under these conditions they dissolve only in good solvents. Since fractionation below the melting point is likely to be very inefficient (147), osmotic calibration of the viscosity law should be especially avoided in such cases.

Anomalous dilute solution viscosities were reported by a number of authors (180 to 185). At concentrations below the customary limits (say 1 gm./l.), the quantity η_{sp}/c was found to increase with dilution, instead of decreasing along the straight line which represents the points at higher concentrations. At still lower concentrations η_{sp}/c decreased again, doubtless because of adsorption of polymer (186). In the most thorough of these investigations, Streeter & Boyer (181) found that the results depended greatly on the techniques employed, varying with the method of dilution, the manner and duration of agitation of the solution, and the time elapsing between preparation of solution and measurement of viscosity. However, for a fixed technique they were highly reproducible. The effect was tentatively ascribed to a very slow untangling (requiring some hours) of the polymer coils, which are considered to be extensively intermeshed at higher concentrations. This hypothesis is surely at variance with current evidence regarding the dynamics of chain configuration, and other explanations such as chemical reaction cannot be excluded. Both Patat & Elias (187) and Mencik & Lanikova (188) failed to confirm the anomaly reported by Batzer and co-workers (184), and suggested that it was due to experimental errors. In this connection, a study by Calderwood & Mardles (189) of the effects of traces of surface-active materials in capillary viscometry is perhaps pertinent. Although the above anomalies do not seriously affect the empirical viscometric determination of molecular weight, which may be accomplished without entering the region of very low concentrations involved, they are sufficiently disturbing from the physical point of view, and should be further investigated.

Wada (190) and Cantow, Pouyet & Wippler (191) reported measurements of dilute solution viscosity at various rates of shear. Their results give further evidence that the deviation from Newtonian behavior is greatest in good solvents and increases so rapidly with molecular weight that it cannot

be entirely neglected, say for M above 10^6, even in the poorest solvents. Furthermore, plots of η_{sp}/c against shear rate often display pronounced curvature at low rates of shear, making extrapolation to the Newtonian limit difficult without an extensive series of measurements. Schulz & Cantow (192) propose to circumvent the difficulty, as far as empirical viscometric determinations of molecular weight are concerned, by restricting capillary viscometers to certain standard dimensions dictated by the kinematic viscosity of the solvent and therefore corresponding to a definite velocity gradient. The "conventional viscosity number" Z_η thus obtained would differ from the Newtonian intrinsic viscosity $[\eta]$, but at least it would be experimentally well-defined and thus useful for empirical purposes. Even from the kineticist's point of view, however, further study of the shear effect is desirable, because its strong dependence on molecular weight in principle offers information about polydispersity. Promise of obtaining experimental results at low shear rates with less tedium than heretofore is given by Eisenberg & Frei's (193) design of a Couette viscometer with an electrostatic restoring torque in place of the usual torsion wire. Chang & Morawetz (194) followed photographically the change of liquid level with time in a capillary viscometer, thus obtaining several points on the viscosity-shear rate curve from a single experiment, and Claesson (195) developed a viscometer in which the change of level is observed interferometrically.

Both extrapolations to zero velocity gradient and attempts to deduce information about polydispersity from the shear-rate dependence of the viscosity are hampered by the incomplete state of current theory. The problem is embraced by Kirkwood's general theory (196) of the hydrodynamic behavior of macromolecules, but explicit calculations from his equations remain to be made. There is great mathematical difficulty in treating adequately the influence of rotatory Brownian motion (197) and of the hydrodynamic interactions between chain elements. In older theories based on the simplified "dumbell" model of a chain [Kuhn & Kuhn (198); Peterlin (199)] the viscosity was found to vary with shear rate only if the molecule possessed an internal viscosity (i.e., frictional resistance within the chain as distinct from that between chain and solvent). However, with a more realistic chain model Bueche (200) constructed a relatively simple theory of the shear effect without introducing an internal viscosity. He recalled that in steady laminar flow the chain experiences a periodic tensile and compressive force, which, if the rotatory diffusion torque is neglected, has a constant circular frequency equal to the shear rate (201). Bueche found that the response of the chain lags behind the force by an amount varying with shear rate, thus altering the viscous losses. Hence, there is a phenomenological similarity between the shear rate in steady-flow experiments and the circular frequency in dynamic viscosity experiments, as was also noted for concentrated solutions and molten polymers by Padden & DeWitt (202), Philippoff (203) and Swann (204). In the free-draining approximation, Bueche found the characteristic relaxation time for the shear effect to have the form

$$\tau = \text{const.}\ \eta_0 M[\eta]/RT,$$

where η_0 is solvent viscosity, M molecular weight, $[\eta]$ Newtonian intrinsic viscosity and RT thermal energy. The empirically noted effects of solvent and molecular weight are clearly reflected in this equation, and the relaxation time is similar to that occurring in dynamic viscoelastic behavior according to the theories of Rouse (205) and Bueche (206). The free-draining model does not give good agreement with experiment, and Bueche obtained considerable improvement with a crude method of introducing the hydrodynamic interactions.

Determinations of long-chain branching from intrinsic viscosities include those of Thurmond & Zimm (169) for styrene-divinylbenzene copolymers, Wales and co-workers (207) for dextran, and Billmeyer (80) for polyethylene. In these studies, the ratio of the intrinsic viscosity of a branched polymer to that of a linear polymer of the same (weight-average) molecular weight was equated to $g^{3/2}$, where g is the ratio of mean square radii (radii of gyration). This relation follows from the Flory-Fox treatment of viscosity (3) if it is assumed that the radius of gyration is always proportional to the effective "hydrodynamic" radius of the particle. Calculations by Stockmayer & Fixman (171) based on Kirkwood's theory of the friction constant (196), indicated that the above relation overestimates the effect of branching on the viscosity, and a tentative improvement was suggested. Kataoka (208) generalized the method of calculating g (209) for various branched structures.

Other hydrodynamic properties.—Williams (210) reviewed methods of studying polydispersity with the ultracentrifuge. Baldwin (211) and Alberty (212) gave improved treatments of sedimentation measurements for polydisperse samples and those with a sedimentation constant depending linearly on concentration. Wales & Van Holde (213) found that for flexible chain polymers the constant k_s in the familiar equation

$$s_0/s = 1 + k_s c$$

for the concentration-dependence of the sedimentation constant, is related to the intrinsic viscosity by the simple formula $k_s \cong 1.66[\eta]$. Combining this result with the Flory (3) treatment of hydrodynamic properties, they arrived at a formula

$$M = 9.2 \times 10^{25} k_s^{1/2} [s_0]^{3/2},$$

where $[s_0]$ is the "intrinsic" sedimentation constant, which even permits approximate calculation of molecular weights from sedimentation measurements alone.

Daune & Benoit (214) and Hosono & Sakurada (215) gave methods for estimating polydispersity from measurements of translational diffusion.

Cerf (216) reviewed the current status of flow birefringence. This phenomenon is closely related to the shear effect on viscosity, and its usefulness for the study of flexible chain molecules is likewise reduced by present incompleteness of the theory. Extrapolation to limiting conditions is also difficult here, and an improved method of doing so, based on the close connection between viscosity and birefringence, was proposed by Peterlin (217).

Miscellaneous Studies

Debye and co-workers (218) reported preliminary results for two methods of detecting the small nonuniformity of concentration produced in a polymer solution by a inhomogeneous electric field. In principle, both the equilibrium distribution and its rate of attainment can be observed, and the information offered by the experiment is therefore similar to that from the ultracentrifuge. The effect was previously observed for smaller molecules by Karagounis (219), and Wales (220) discussed its possible utility for high polymers.

Spencer's method (221, 222) for the rapid though crude determination of polydispersity was applied to polyvinylchloride by Matsumoto (223) and to GR-S by Golub (224). The latter concluded that lack of equilibrium in the precipitations causes the method to have doubtful value.

Schulz & Sabel (225) described a technique for isolating polymer samples involving addition of solution to precipitant in the form of a fine spray, thus reducing occlusion of solvent.

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COLLOID CHEMISTRY[1,2]

Exclusive of High Polymers

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Even with the initial exclusion of those areas of colloid chemistry concerned with adsorption of gases, high polymers, proteins, chromatography, ion exchange, and membrane electrodes, some 715 papers appeared in this field during 1954 in addition to an extensive trade literature. Necessarily, this review is restricted in nature, treating only Gels and Greases, Micellar Solutions, Surface Chemistry of Condensed Systems, and Aerosols, topics in which one or another of the authors have been interested for a number of years. Since much important new work is thereby excluded the detailed report is prefaced by a brief listing of some of the useful books and reviews which have appeared during the last year.

Books and reviews.—A useful encyclopedic review attempting to cover the whole field of colloid chemistry was prepared by Broughton (1). Theoretical rheology and the general field of relaxation phenomena of both dielectric and mechanical nature were extensively treated in two symposia held at Marburg, and reported in the December, 1953 and August, 1954, issues of *Kolloid Zeitschrift.* A Debye 70th Birthday Symposium reported in the August, 1954, issue of the *Journal of Physical Chemistry* provided a group of papers on the behavior of polyelectrolyte molecules and the theory of light scattering. A Symposium on Solutions of Electrolytes, reported in the September, 1954, issue of the *Journal of Physical Chemistry*, dealt partly with polyelectrolyte molecules and partly with the electrolytic properties of protein solutions. Evidence that not all molecules in a "pure" protein are identical was presented by Colvin, Smith & Cook (2). Liesegang phenomena were treated by Stern (3) and the phase contrast technique and its applications by Walter (4). Two other important symposia were also reported during the year, one dealing with Flow through Porous Media in *Industrial and Engineering Chemistry*, June, 1954, and the other on the Physics of Particle Size Analysis in Supplement 3 of the *British Journal of Applied Physics*, 1954.

Many books of colloidal interest appeared during the last year. Flow phenomena were treated from many different points of view by Hermans (5), Gross (6) and Harrison (7). Chromatography continues to receive much attention with different aspects emphasized by E. and M. Lederer (8), Smith (9) and Turba (10). Electron microscopy and its applications were described by Hall (11), and in the bound report of an International Congress at Ghent,

[1] The survey of literature pertaining to this review was concluded with November, 1954.

[2] The section on Aerosols was kindly contributed by Dr. Harry L. Frisch, also of the University of Southern California.

Belgium (12). A valuable bibliography of work on electrophoresis was prepared by Henley (13). New approaches to the study of surface films were described by Sobotka (14) and the applied field of detergency in books by Harris (15) and Dunod (16). A most comprehensive summary of the theory and art of grease manufacture and application was prepared by Boner (17). Vol. II of *Der Physik der Hochpolymeren* (18) has a series of excellent articles on the behavior of dissolved macromolecules. Understanding of protein chemistry was facilitated by the publication of a monograph by Neurath & Bailey (19) and of a conference on proteins held in Brussels (20). Finally, mention should be made of the publication in excellent English translation of the collected papers of Debye (21), including his fundamental work on x-ray scattering, dipole moments, electrolytes, and light scattering.

Gels and Greases

P. H. Hermans (22) defines a gel as a two-component system exhibiting the mechanical properties of the solid state, within which both dispersed constituent and dispersion medium are continuous. The term "continuous" in this definition is the key to correlating recent studies interpreting gel properties in terms of an inferred structure inasmuch as gels are formed through the building of such continuous structures by aggregative processes from initially independent units. Attention then comes to focus on the density of the junction regions, their strengths, and the mechanism of the cohesion between the "monomeric units." The dispersed component can be regarded as a single, essentially infinite "molecule" or, if this word be distasteful in view of the variegated types of linkages between monomeric units, a single infinite floc or aggregate. A conspicuous advance in understanding the behavior of greases results from the work of Hutton & Matthews (23) on the rheology of sodium and lithium greases at very low stresses. This work suggests that a grease may be regarded as a gel of the same type as that formed by a crosslinked polymer with the added complication that a broad spectrum of junction strengths exists, many of which are so weak that "depolymerization" of the infinite floc into subsidiary gel lumps occurs during flow to an extent strongly dependent on the rate of shear.

This developing concept, which has so far received only qualitative formulation, appears capable of correlating a number of different types of earlier observations. The decrease in grease consistency with decreasing length/width ratio of ultimate fibers found by Moore & Cravath (24) is thus explicable in terms of a larger density of crosslinks. Confirmation of the idea that flow in greases is accompanied by the disruption of aggregate structures comes from the work of Bondi (25) who found that the electrical resistance of gels of carbon black in mineral white oil increases with increasing shear rate. The very rapid changes in dielectric constant with change in shear rate reported by Bondi & Penther (26) are attributed by these authors to particle orientation due to elastic deformation of the gel lumps. A second type of particle orientation demonstrated by Vold *et al.* (27) in x-ray diffraction

studies of deformed grease blocks remains unaltered in resting greases for long periods and is presumably due to alignment of individual fibers freed of constraints during the flow process.

Quantitative development of this hypothesis evidently requires accumulation of data on the actual sizes and configurations of grease fibers and on the origin and magnitude of their interactions. The current state of information on the former subject has been ably reviewed by Boner (17) in his book, in the chapter on "Structure and Theory" containing a bibliography of 111 references, extending to 1953. Evidence has been found by Robert (28) that the ultimate fibrils in soap greases grow by recrystallization even in hydrocarbon media at room temperature. Interest has been shown in the occurrence of ropelike aggregates revealed by the electron microscope in soap greases [see ref. (17) p. 18 for a fine example]. Vold *et al.* (27) believe that these are less abundant in intact greases viewed in thin sections than among fibers freed from greases by solvent dilution.

Information about the binding between dispersed particles in gels and greases has hardly passed the speculative stage. The point of view that bound solvation shells and relatively long-range interaction between spatially separated particles is important in aqueous bentonite gels has been recently reiterated by Forslind (29), by Jordan & Williams (30) for oleophilic bentonites, and by Greenwald & Brown (31) for aqueous gels of polyoxyethylene ethanols. Bondi (25) found that petroleum sulfonates effective in stabilizing dilute dispersions of carbon black in oil also lower the yield stress and increase the electric resistivity of carbon black gels, suggesting that electrical interactions due to adsorbed ions of the type found by van der Minne and Hermanie (32) may be important [see also Boonstra & Dannenberg (33)]. A beginning has been made by Vold (34) in evaluating the possible contribution of generalized attraction of the van der Waals type. Scott, Goldenson & Bauer (35) succeeded in showing through infrared studies that partial liquefaction of aluminum soap gels in benzene by addition of *m*-cresol is accompanied by rupture of *Al-O-Al* cross links but that the *OH* absorption is unaffected. In some gel-like systems (reinforced rubbers) interparticle binding may occur by adsorption of segments of the same polymer chain according to Riseman & Harper (36). Progress is also being made by Harvey (37) in studying model gels formed of suspensions of magnetized iron particles.

It is becoming apparent that valuable information about the behavior of gels is to be obtained by studying the properties of dilute sols of the same particles. Buzágh (38) found that the tensile strength of bentonite films was minimal when the films were prepared from suspensions at salt concentrations yielding thixotropic sols. There is also renewed interest in sedimentation volume as an investigative tool. Buzágh (38), studying montmorillonite suspensions of 4 and 15 micron particle size, found the finer suspension gave the larger sedimentation volume, and that on addition of electrolyte the sedimentation volume reached a maximum at the isoelectric point. Large sedimentation volumes are taken as evidence of stronger forces of attraction

between the particles. Ross & Schaeffer (39) and also Eggleton & Puddington (40) are of the opinion that the interparticle bonds in relatively coarse sedimenting suspensions are closely connected to wetting phenomena, incomplete wetting being qualitatively correlated with particles which can reduce their area of contact with their environment by mutual adhesion. The effect of electrolytes in increasing the sedimentation volume found by Ruston & Halla (41) for clay-quartz mineral suspensions suggests that interparticle forces of other sorts are also involved. The time would appear to be opportune for a good statistical analysis of the relation between sedimentation volume and interparticle interactions, since such flocculent sediments are closely analogous to weak gels, but such a treatment has not yet appeared.

A paper by Eldridge & Ferry (42) is valuable both for its approach and for its essential result, namely, that the crosslinks in gelatin gels are due to hydrogen bonds with 10 to 45 such links per junction point, the number varying with the gelation temperature. These workers determined the gel melting point as a function of concentration of five degraded gelatins with weight average molecular weights varying from 33,000 to 72,000. In order to relate the number of crosslinks at the gel point to molecular weight, they were obliged to rely on the well-known Stockmayer relation (43) which neglects the sterility of internal crosslinks for extending the growing aggregate. A somewhat different picture of gelation in gelatin has been advanced by Boedtker & Doty (44) and Beyer (45) in which aggregate formation leading to units having the mean shape of random coils occurs, actual gelation resulting from crosslinks of a crystalline nature between these aggregates. The crosslinks are readily broken on dilution but the aggregates dissociate slowly enough to permit determination of their size and shape by standard light scattering and viscometric techniques. The kinetics of gelation does not seem to follow the Stockmayer equations in that in its latter stages aggregate growth is not as rapid as predicted. Bourgoin & Joly (46) also find on the basis of streaming double refraction that aggregate formation is a precursor, and probably a separate process, from the crosslinking leading to mass solidification both in gelatin and gum arabic. Schurz (47) presents evidence (from rheological data) that also in viscose solutions aggregation of the cellulose chains occurs as the concentration increases. Similarly Pilpel (48) explains gel formation in soap solutions in terms of a postulated aggregation of existing micelles into elongated interlocked structures. One might expect that application of statistical theories of cluster formation and of crosslinking reactions, developed primarily for imperfect gases on the one hand and polymer systems on the other, to a quantitative description of the gelation process would be very fruitful, but this has not yet been done.

On the experimental side, mention should be made of the increasing interest shown in ultrasonic radiation and similar mechanical methods as investigative tools (49, 50), a critical review of which is not attempted here. A particularly interesting study is that of Nakagaki, Ishibashi & Sakata (51, 52) who found that aggregate structures in sols of mercury sulfosalicylate and

vanadium pentoxide were disrupted by ultrasonic vibrations (frequency 610 kc.) but recovered in time, parallel changes occurring in the structural viscosity. Likewise, the comparative study of light scattering in gelatin gels, and in dispersions of the gel-forming aggregates by Boedtker & Doty (44), seems promising for developing an understanding of the nature of the interactions between aggregates.

Coacervation.—Even though coacervation is a different phenomenon from gel formation in that it always involves a phase separation, while gels may behave thermodynamically as either two-phase or one-phase systems, the underlying considerations on a molecular level are similar. The dispersed material in the colloid-rich phase may be continuous as in the limited swelling of polymers, an interesting treatment of which has been given by Krigbaum & Carpenter (53) and in soap coacervates as suggested by Cohen, Hiskey & Oster (54) or discontinuous as in the case of tobacco mosaic virus. Booij (55) is beginning to develop a significant application of theories of coacervation to the structures and permeability of biological membranes. Silberberg & Kuhn (56) have contributed to a new method of study, showing that phase separations analogous to coacervation may be inhibited in a flow field, the rate of supply of mechanical energy being sufficient to prevent aggregate formation.

Micellar Solutions

The properties of solutions of association colloids have been extensively studied in the last few years, utilizing not only the classical methods but also the experimental tools and interpretive techniques developed in the fields of polymer and protein chemistry, and clearing up much of the confusion existing at the time of Williams' review (57). At the risk of over-simplification and a possibly callous neglect of some contrary indications, it can be said that the present evidence points to the formation with increasing concentration of nearly monodisperse, effectively spherical aggregates over an extremely narrow concentration range (c.m.c., the critical micelle concentration). At higher soap concentration (generally above 6 per cent) there is a still further increase in micellar size and a change in shape to a laminar or cylindrical form. The c.m.c. is strongly dependent on the ionic strength of the solution, added electrolyte also increasing the size of the micelles. The effective charge on the micelle is probably to be understood on the basis of exactly the same considerations which determine the distribution and degree of kinetic independence of counter-ions around any other charged particle of colloidal size. The physical chemical properties above the c.m.c. can be interpreted as are those of polyelectrolytes, the dissociated fraction behaving like added simple salts, but with the simplification that changes in shape like the uncoiling of polymer molecules need not be considered, and the complication that the micellar size is affected by salt concentration.

However, conflicting results continue to be obtained. Granath (58) found (by combining diffusion and sedimentation data) frictional coefficients vary-

ing from 1.2 to 5.2 times those calculated for spheres of the same molecular weight, the value being higher for a given soap with increasing ionic strength. Anacker (59) contends that the molecular weights (of the order of 20,000) obtained for solutions of octyltrimethylammonium salts of octanesulfonic and decanesulfonic acids in water and KCl solutions are incompatible with the assumption of spherical shape because of the implied submersion of polar groups in the interior of the micelle. There is no doubt from the work of Dervichian, Joly & Titchen (60) (viscometry, flow birefringence) that highly asymmetric particles exist in very concentrated soap solutions but these may possibly be chain-like aggregates of smaller spherical micelles. Cohen, Hiskey & Oster (54) postulate similar aggregation as the result of van der Waals attraction. The apparent conflict between the x-ray evidence and the presumption of spherical micelles appears to be resolved by the work of Brady (61), who showed that the very long spacings could be interpreted alternatively as mean distances of closest approach of spherical micelles rather than as the repeat distance within a laminar micelle.

Ekwall (62) criticizes the focussing of attention on a single c.m.c. and presents evidence that departures from ideal behavior interpretable as association of monomers can occur at much lower concentrations and that the c.m.c. itself is a concentration range of substantial width (as much as twofold for sodium oleate). He likewise believes that changes in properties due to micellar interaction begin to occur over a narrow concentration range (a second c.m.c.). A considerable fraction of his results may be explained on the basis that third components (hydrolysis products, solubilized materials used as investigative tools) affect the micellization process, as pointed out by McBain & Das Gupta (63). The results of Spring & Howard (64) on solubilization phenomena in potassium laurate-lauric acid solutions indicate two kinds of micelles in such multicomponent systems.

A number of new experimental results on the molecular weights of micelles are available from the sedimentation studies of Granath (58). This appears to be one of the first successful applications of ultracentrifugal techniques to soap solutions, in which partial molal volumes (cf. 65) vary with concentration so that the micelles sediment sometimes toward and sometimes away from the center of rotation. Results for some commercial detergents have been published by Mankowich (66) on the basis of light scattering, but their derivation from the actual data is open to question. In addition to the problematic effect of impurities, the validity of extrapolating the usual Hc/τ plot to infinite dilution instead of to the c.m.c. is doubtful. Hutchinson (67) suggests that extrapolation should be made to infinite dilution but in high salt concentration to neutralize the effect of the micellar charge, an approach which is unsound because of the known dependence of micellar weights on salt concentration, if not on other grounds. In a recent paper Mysels (68) gives an excellent discussion of the effect of the charge on the micelles on the course of the curve of Hc/τ, and shows how the results can be interpreted to yield values of micellar charge as well as micellar weight data.

Factors controlling the size of the micelle are still not well understood. The original Debye picture (69) giving an optimum size as a result of balancing electrostatic repulsion and van der Waals attraction does not account adequately for the apparent monodispersity nor for micellization of nonionics. Ooshika (70) suggests balancing surface energy and electrostatic repulsion. A similar approach is employed by Shinoda & Kinoshita (71) who take into account both van der Waals cohesion and surface energy, and by Persoz & Rosano (72). Studies of the effect of solubilized materials on micellar size, and on the viscosity and conductivity of solutions have been reported by Bose (73), Flockhart & Ubbelohde (74), and Heckmann (75). While this approach is as yet only qualitative, it appears to be very promising unless the solubilized materials themselves greatly modify the packing of detergent ions.

The c.m.c. is surely related to the aggregation number, added salt lowering the one and increasing the other. Experimental results obtained for the c.m.c. by the dye solubilization method, however, have recently been criticized by Hiskey & Downey (76) on the grounds of a demonstrable association between surfactant ions and oppositely charged dye ions. Kushner & Hubbard (77) have examined the bubble pressure method of determining the c.m.c. pointing out that the maximum bubble pressure is essentially a surface tension measure, and thus subject to the same notorious sensitivity to traces of impurities, and also not necessarily directly related to bulk micellization. On the theoretical side, Shinoda (78, 79) has expanded the theoretical derivation of the empirical relations between c.m.c. and (*a*) chain length, (*b*) salt concentration, (*c*) alcohol concentration, and (*d*) composition in mixed soap systems. He attempts to take into account modification of the chemical potential of the micellized soap due to the effect of the uncharged species on the electric double layer around the micelle and to the dilution effect, alcohol and soap in the micelle being treated as a regular solution.

Contributions to the thermodynamics of micellar solutions have been made by Stauff (80) and more recently by Stigter (81). Both these treatments attempt to calculate the free energy change associated with the formation of one mole of soap in the form of micelles of fixed aggregation number, taking into account interaction of the charged micelle with its atmosphere of gegenions, and also the entropy of mixing. The former is calculated on the basis of a hypothetical process in which the monomers are first assembled and the charge on the assembly gradually increased to its final value. Stigter's process, which allows for variation in the potential at the surface of the micelle, seems to be more nearly correct, although as Stigter himself points out the subsequent use of the Debye-Hückel approximation will lead to too large values of the electrical contribution to the free energy. Stauff also derives an expression for the entropy of the association process. It is well-known that the distribution of micellar sizes, and the concentration range over which micellization begins to occur, are too broad when calculated on simple mass action principles. Stigter's work has not yet been carried to the point of evaluating its contribution to this problem, but has instead been directed

towards experimental tests of the validity of the treatment of electrical interactions. A treatment of conductivity data (82) leads to an interpretation of so-called anomalous behavior (maxima in the equivalent conductance-concentration curve) on the basis of the existence of a distribution of micellar sizes. A derivation of micellar size from dependence of the c.m.c. on salt concentration leads to aggregation numbers which are substantially smaller than those obtained by light scattering on the same material (sodium dodecyl sulfate). Most interesting is the interpretation of electrophoretic mobility data (83, 84) obtained by the ingenious dye tracer method of Hoyer, Mysels & Stigter (85), from which it has proved possible to calculate the quantity of water entrained by the hydrodynamic micelle (micelle plus closely adherent gegenions and water), the zeta potential, the micellar charge, and the potential at the surface of the unhydrated micelle. The low degree of ionization found (30 per cent for sodium dodecyl sulfate) led to the suggestion of a "rough micelle" with hydrated gegenions bound in the micelle between polar anionic groups.

Lifson & Katchalsky (86) and Hayman (87) have treated the electrical free energy due to the gegenion distribution around a charged cylindrical polyion. Although developed primarily for application to polyelectrolytes, these papers are of potential interest in relation to the difference in free energy between cylindrical and spherical micelles of the same aggregation number. In polyelectrolytes most attention has been paid to the influence of charge effects on the extension of the polymer chain (88 to 96), so far as structure is concerned. Treatment of properties such as osmotic pressure, light scattering, and viscosities of polyelectrolytes are so closely related to corresponding treatments for uncharged polymers as to be properly excluded from extensive review here.

The obvious difference between polyelectrolytes and micelles is the relative mobility of polymer segments contrasted with the cohesion of the paraffin chains in micelles. Strauss & Gershfeld (97) studied copolymers of 4-vinyl-N-ethyl and N-dodecyl-pyridinium bromide finding a progressive decrease in reduced viscosity with increasing dodecyl content as would be expected. Saito (98) reports association complexes of polyelectrolytes with detergents having somewhat similar properties.

Association to micelles occurs also with soaps in nonaqueous media. Theories of their structure have been presented by Singleterry *et al.* (99, 100) and Winsor (101). In a recent paper Honig & Singleterry (102) conclude from rheological data that in strictly anhydrous media sodium phenyl stearate forms chain-like aggregates rather than small compact micelles, which revert to a much more compact structure with traces of polar additives. Further addition of polar additive results in the formation of ramifying aggregates of these micelles. Bromilow & Winsor (103) suggest there are two kinds of compact micelles, with polar groups in the interior in hydrocarbon solvents and on the exterior in polar solvents, with a transition region in mixed solvents leading to actual phase separation (liquid crystalline phases)

in which the micellar aggregates are extended and of an orderly structure. Both pictures are probably as nearly correct as such qualitative descriptions can be, and suggest the variety of types of behavior that may be found in such systems. For example, Rao & Palit (104, 105) find a maximum in the solubilizing power of soaps in mixed organic liquids for water as a function of solvent composition. Likewise, it is well-known that the solubility of soaps is many fold greater in mixed solvents than in either pure component.

Surface Chemistry of Condensed Systems

Since reviews of *Surface Chemistry and Catalysis* have been confined largely to a consideration of gaseous adsorption it seems useful to present here a survey of certain other aspects of colloid chemistry in which adsorption plays an important role.

Adsorption at the air-water and oil-water interfaces.—The development of radio-tracer methods for moderately accurate studies of adsorption has stimulated renewed discussion of the proper application of the Gibbs equation. A modification of previous methods in which the tracer is incorporated directly in the surfactant molecule has been presented by Steiger & Aniansson (106) who found that Bi-212 is coadsorbed with sodium lauryl sulfate in proportionate amount. Discussion centers around the magnitude of the factor n in the equation $-d\gamma = nRT\Gamma d\ln c$. Essentially equivalent discussions have been given by Pethica (107) and Cockbain (108). In dilute solutions of a strong surface-active electrolyte with no added salt $n = 2$. In the presence of added salt, some nonthermodynamic assumption is necessary to define the value of n. Various forms of equations of state result, depending upon the particular model of surface considered. At high electrolyte concentrations and low surfactant concentrations n approaches unity experimentally. Davies (109) describes results which show that equations of state based on describing interaction with a Gouy-Chapman double layer beneath the surface may fail at high electrolyte concentrations due to penetration of gegenions into the surface layer. Judson *et al.* (110) report tracer studies with the sulfate counter ion tagged which seem to confirm previous suggestions that hydrolysis may occur in the surface layer but suggest also the more reasonable interpretation that this should be regarded as preferential adsorption of hydroxyl ion into the layer of counter ions rather than adsorption of an undissociated species as was once suggested even for the strong acid, dodecyl sulfonic acid. Roe & Brass (111) find no evidence for preferential adsorption of lauric acid from potassium laurate solutions so long as the pH is above ten. At surfactant concentrations above the bulk c.m.c., adsorption at the air-water interface increases enormously according to Judson *et al.* (110) and also Ruyssen & Maebe (112). There is as yet no evidence to show whether this new phenomenon is spontaneous multilayer formation or adsorption of whole micelles.

Structure in spread films.—With respect to equations of state for the adsorbed film (or for spread monolayers) evidence is increasing that molec-

ular interactions preclude application of any such simple equation as $\pi(A-A_0)=nRT$ at even quite low surface pressures. Surface balances with a sensitivity of 0.001 dyne have been constructed, as by Allan & Alexander (113), who find that molecular weights from extrapolation of curves of πA versus A may be in error, even when extrapolated to zero pressure from pressures of a fraction of a dyne and areas of the order of square meters per gram, by 15 to 30 per cent for molecular weight ranges of 20,000 to 50,000.

Use of force-area curves and surface potential measurements to study the behavior of the molecules themselves from their behavior in films continues to develop (114 to 117). Davies (118) finds from surface potential measurements that the ϵ-NH_2 groups of lysine residues tend to enter the nonaqueous phase, confirming earlier suggestions that orientation in interfaces may affect enzymatic activity by withdrawing or presenting particular reaction sites. With polymer films formation of bonds during film compression [Müller (119), Schuller (120)] leads to hysteresis phenomena and the absence of sharp transitions between film types. Dean, Hayes & Neville (121) find that adsorption of organic vapors on "patchy" films of stearic acid expands the surface micelles to form a uniform film.

Interaction with substrate of spread films has also been investigated from the point of view of applications. In a series of papers Thomas & Schulman (122) report not only the well-known soap formation in fatty acids spread on salt solutions but film solidification at higher areas due to hydrogen bonding in the substrate with complex soaps. Similarly, Glazer (123) shows that the increased collapse pressures of spread films of some ethoxylin resins with increasing hydroxyl content of the resin reflects the role of hydrogen bonding in the adhesion of the film to its substrate. Hemolysis and bactericidal action of surfactants have been associated with interaction of the adsorbed film with the cell membranes forming mixed films by Pethica & Schulman (124) and Ross *et al.* (125, 126). Similar mixed films are found by Schulman & Leja (127) to be important in the interaction of so-called "frothers" and "collectors" in flotation. Hydrogen bonding involving an amide group is shown by Ellison & Zisman (128) to influence the wettability of nylon films by hydrogen-bonding liquids, and other wetting phenomena are similarly rationalized.

Adsorbed films on solid surfaces generally are obviously influenced by heterogeneity of the solid surface. While this is by no means a novel idea, the development of the electron emission microscope has added greatly to the tools available for study of the phenomena as in the interesting study of the adsorption and mobility of barium on tungsten by Drechsler (129). Studies of the adsorption of water and other vapors on a variety of notoriously heterogeneous surfaces [charcoal by McDermot *et al.* (130), "graphon" by Young *et al.* (131), chabasite by Barrer & Rees (132)] all show evidence of adsorption by clustering about preferred sites. Schulman & Leja (133) believe that stabilization of emulsions by solid powders requires that the surface be partly wet by oil and partly by water, a condition which may possibly be

brought about by surface inhomogeneities. Bowers, Clinton & Zisman (134) advance the interesting idea that the failure of many surfactants to form lubricating films on nylon is due to the wide separation of the polar amide groups forming the adsorption sites. Such structural features are sure to affect the use of adsorption techniques in surface area measurements, which have been ably reviewed by Moll (135).

Evidence that deposited "monolayers" of stearic acid exist on metal surfaces as clumps and patches (except when strongly chemisorbed as on copper) is found in the phenomena of monolayer overturn and transfer from one metal piece to another placed in almost haphazard contact with it as described by Rideal & Tadayon (136). Some of the adsorbed acid molecules apparently climb up onto such patches and diffuse across them more rapidly than on the bare metal to reach isolated chance contact points at which the transfer process can occur.

Surfactant adsorption at liquid-liquid interfaces is apparently more nearly uniform. Maron *et al.* (137, 138, 139) and also Rakshit (140) find that particle size in emulsions may be reasonably estimated from total surface area on the assumption of a uniform monomolecular film at saturation, although difficulties arise in some cases [Morton *et al.* (141)] Wiley (142) found that in coarse oil-in-water emulsions droplets grow to a limiting size determined by the condition that the amount of added stabilizer be just sufficient to form a complete monolayer. The actual stability of emulsions to coalescence, however, appears to depend not so much on the existence of such films as on specific film-substrate interaction [Cockbain & McRoberts (143); Neogy (144)].

Kinetics of surface film formation.—Surface films are apparently formed and reach equilibrium in times measured in milliseconds. Nevertheless, methods have been available for several years to study both rate of change of surface tension (145) and surface potential (146). The phenomenon may be of practical importance (see later under detergency, and also Evans (147) in connection with flotation). However, the theory of the effect appears to be in a fine state of confusion. The prevailing concept has been that observed rates of surface tension drop were necessarily smaller than those calculated from diffusion theories, because both charge effects and steric effects combine to produce a potential barrier at the interface which retards normal diffusion. Lange (148), who worked with a series of technical wetting agents; Posner & Alexander (149), who investigated some alcohols and anionic and cationic detergents; Quintin & Biro (150) who measured interfacial tensions, are all inclined to discuss their experimental results in terms of the nature and origin of this barrier. Fordham (151), however, points out that previous theory assumes the validity at all times of the Gibbs equation relating surface tension and surface excess, or of some equation of state for the film. Actually, none of these relations can be valid because the concentration gradient in the bulk solution in the neighborhood of the interface affects the chemical potentials of the diffusing species in the bulk solution which are

taken as constants in applying the above ideas. He sets up an analogue of the Gibbs equation in which the chemical potential in the surface is set equal to the instantaneous chemical potential in the immediate subsurface region and obtains calculated rates which are slower than those observed experimentally, suggesting that the discrepancy is due principally to the approximations needed in the solution of his equations. Somewhat similar calculations have been made by Defay *et al.* (152, 153).

Electric double layer.—In view of the recent review by Troelstra (154) it seems unnecessary here to do more than mention briefly the outstanding progress that has been made in this field during the past year. The differential capacity of the double layer on mercury in solutions of sodium fluoride, chosen because of the apparent total absence of specific chemisorption effects, has been accounted for in great detail by Grahame (155) and by Macdonald (156). Treatments of cases in which such chemisorption occurs have been presented by Grahame & Soderberg (157) and by Devanathan (158, 159). The numerical solution of the complete Poisson-Bolzmann equation for the distribution of potential about a charged spherical colloidal particle presented by Hoskin (160) is sure to be of great value.

On the experimental side, the paper of Overbeek (161), demonstrating the complete thermodynamic equivalence of the various electrokinetic phenomena, and the various experimental papers showing the extent to which equivalent values of the zeta potential may actually be realized by the differing techniques (162, 163, 164), are of interest. The effect of adsorbed surfactants on the electrocapillary curve and on polarographic behavior is reported by Bonting & Aussen (165) and Gupta (166). This effect has been developed into a novel method for determining adsorption at interfaces of small area by Hansen & Clampitt (167). Hubbard & Reynolds (168) use the same phenomena to detect micelle formation, finding discontinuities in the diffusion current as a function of concentration at the critical micelle concentration.

Some factors involved in detergency of solids.—Despite the complex nature of practical detergency and its voluminous industrial literature, the fundamental problem involved can be stated quite simply. What is the actual distribution of component one ("soil") between component two ("substrate") and component three (deterging medium)? This problem is to be analyzed taking due cognizance of the probable effects of the colloidal structure of each component as well as its chemical composition, and of the fact that a given system is not necessarily in equilibrium or even in a stationary state at the instant of measurement, and that its instantaneous condition may depend on the level of mechanical agitation as well as on initial composition and colloidal structure.

Natural subdivisions can be made according to the nature of the three components. In most practical investigations relating to fabric detergency the soil is an oil-based suspension of a carbonaceous (sometimes siliceous) material while the deterging medium is an aqueous solution of a technical

detergent. The experimental results are obtained in the form of an over-all measure of "effectiveness," meaning that it is desired to concentrate the soil in the deterging medium thus removing it from the surface. Commonly, the soil content of the detergent medium, or some quantity related to it, and the soil content of the substrate, or some quantity more or less related to it, are the quantities measured. Extensive practical investigations of this sort, with attempts to establish semiempirical but none the less useful correlations between effectiveness and easily measurable properties of the detergent have been added during the year by Baumgartner (169), Ballun *et al.* (170), Jellinek & Mayhew (171), Vaughn *et al.* (172), and Mankowich (173) to the extensive volume of existing literature on the subject. The excellent summary by Schwartz & Perry (174) is still unsurpassed for purposes of general orientation in this field.

One of the greatest difficulties in this kind of work, and especially in more fundamental studies, is the problem of measurement and control of pertinent variables. Of these, the significant role of mechanical work has not yet been adequately evaluated. The introduction of the Kubelka-Munk equation relating soil deposition to reflectance of the soiled fabric by Bacon & Smith (175), together with the evaluations of its applicability by Reich *et al.* (176), and more recently Harris *et al.* (177), provide an easy and reliable method of determining soil content of the substrate when the equation is applicable. Recent studies by Phansalkar & Vold (178), however, show that this is specifically not the case in regions of greatest theoretical interest in which the detergent is affecting the degree of dispersion of the soil particles.

One of the central problems in detergency of solids is the question as to whether the soil is held on the surface by forces akin to those governing adsorption of molecules or whether a mechanism of mechanical entrapment in surface rugosities is more important. Compton & Hart (179) have been strong proponents of the latter view while Goette (180), inclining to the former, presented an extensive review of the importance of the zeta potential in detergency.

Since the detergent is adsorbed on both fabric and soil, measurement of the extent of adsorption is useful irrespective of the various theories concerning the role of the adsorbed material. Notable experimental results have been reported by Weatherburn *et al.* (181), Meader & Fries (182), and Corrin *et al.* (183). However, in a recent study, Vold & Phansalkar (184) find that soil deposition, while it decreases regularly as adsorption increases with increasing detergent concentration at low concentrations, levels off at a concentration having no relation to any obvious critical region of the adsorption isotherm.

The most naive role to assign to adsorbed detergent is that of blocking sites otherwise available for soil-fabric attachment, or forming mechanically rigid films of small mutual cohesion on fabric and soil. A second hypothesis pertinent to liquid soils is that the adsorbed detergent reduces the interfacial tension between water and fabric to a value below that between oil and fabric.

Unfortunately, the measurable quantity, oil-water interfacial tension, does not define either of these separately. Nevertheless, work is still proceeding in the attempt to develop practical predictions of detergent effectiveness on this kind of hypothesis [see, for example, (185)]. Burcik (186) suggests that it is not the equilibrium interfacial tension but its actual value at the instant of separation of the soil which is important. This will be lower the greater the rate of approach to equilibrium. An interesting parallel is found between effect of temperature, electrolytes, etc., on detergency and rate of surface tension lowering.

Another somewhat more sophisticated but also incompletely successful interpretation is based on the idea that deterging solid soils is similar to a deflocculation process, with the stability of the deflocculated system—clean fabric and suspended soil—governed by the same principles which determine the stability of lyophobic colloids. Stackelberg *et al.* (187) find that small concentrations of electrolytes first increase the zeta potential of hydrophilic fibers in solutions of alkyl sulfates, presumably due to increased adsorption of detergent ion, and then at higher concentrations decrease it, showing good correlation with washing effectiveness. Wijga (188) presents a similar hypothesis considering the zeta potentials of both fiber and soil. Vitale (189) finds that electrolytes increase soil redeposition (with cotton, syndets, and aquadag) which is in accord with a presumed lowering of zeta potentials. Hazel *et al.* (190) find somewhat similarly that salts reduce the time required for adhesion of phosphor powders to glass by reducing the repulsion between the surfaces through lowering of zeta potentials. On the other hand, this mechanism is presumably inapplicable to nonionics; more importantly, it seems not to account for the relative ineffectiveness of cationics which Doscher (191) found to give high positive zeta potentials to both carbon and cellulose. On the other hand, among the recent careful measurements of zeta potential on various fibers by Stanley (192), is the observation that at least one cationic (dodecyl pyridinium bromide) gives a zeta potential which, in changing from negative to positive as its concentration and thus adsorption increases, becomes zero at 2×10^{-3} M (circa 0.05 per cent). This is not far below washing concentrations. Given that adsorption equilibrium may not be complete, the actual zeta potentials in the case of cationics and cotton can conceivably be too low to effect substantial particle-soil repulsion.

This entire development is based implicitly on the idea that soil and substrate will cohere in the absence of some specific repulsive mechanism. Generalized van der Waals attraction of the type adduced in the Verwey-Overbeek theory (193) has not been considered quantitatively as a source of this cohesion. However, it is a consequence of this theory that sols of very small particles are more difficult to stabilize than sols of large particles. The effect of a detergent in dispersing soil aggregates may thus serve to decrease the stability of the system clean cloth—dispersed particles. A suggestive variant of this idea is advanced by Jordan (194) in accounting for the increased

tendency of dust particles to adhere to surfaces as their particle size decreases.

Great interest, without definitive result as to solution, exists also in the problem of the mechanism by which carboxymethylcellulose improves the stability of the deflocculated systen, *i.e.*, retards redeposition of soil. In this connection, the report of Nieuwenhuis (195) on the adsorption of carboxymethylcellulose by cotton contradicts the work of Stüpel & Röher (196) who find it extensively adsorbed on fatty soils but not on cotton or silk. However, the method of the latter authors for detecting adsorbed carboxymethylcellulose through its ability in turn to adsorb a fluorescent dye may well account for the discrepancy. Heller & Pugh (197) found a sharp increase in the gold number of sols protected with polyethylene glycols as a function of molecular weight, which suggests that the protection may be basically steric in nature, the extension of the adsorbed polymer preventing approach of soil particles to within range of the van der Waals attractive forces.

Surely, most of the above factors are involved in detergency, but a satisfactory elucidation of their relative roles has not yet been given.

Aerosols[2]

Recent general references reviewing this rapidly expanding field of colloid chemistry are the chapters by Richardson and Green in the book edited by Hermans (5), a report on a conference on particle size analysis by Lang (198), and on dusts, smokes, and powders by Eichorn (199). Only problems involving aerosol production and evaporation, aerosol behavior in external force fields, and size and size distribution of aerosol particles are considered here.

Growth, production, and evaporation of aerosols.—A number of new methods for producing a monodisperse liquid aerosol having a particle radius of a micron or less have been reported recently. Neubauer & Vonnegut (200) investigated aerosol production from liquids such as water, aqueous HCl and salt solutions which are atomized from positively charged capillary tubes under S.T.P. conditions. An increase in the conductance of these solutions produces smokes of particles of larger diameter which are no longer monodisperse. Blanchard (201) showed that when bubbles of air of a given size burst at the air-water interface an upward jet of water is produced by the collapse of the bubble cavity, which subsequently disintegrates to form drops. The size of the drops thus formed is a function of both the height of rise of the drops and the size of the original air bubbles, and allows production of monodisperse droplets down to a diameter of 2μ. Schaefer (202) investigated the formation of ice crystals by the rapid expansion of moist air contained in a glass sphere. The maximum observed number of ice crystals was found to be 10^{11} crystals per cc. which implies that the nucleation mechanism in this system does not depend on the presence of foreign particles.

Further extension of the theory of the diffusion-controlled growth of an aerosol suspended in a medium at rest has been carried out by Frisch & Col-

lins (203), taking account of both the initial smallness of the radius of the growing aerosol in comparison with the mean free path of the diffusing species, and the possibility that the accommodation coefficient for condensation differs from unity (204). The resulting growth law is no longer "parabolic," i.e., if R is the radius, t the time, and p the pressure these authors find $dR/dt = A/(1+BpR)$ where A and B are constants, the pressure dependence shown having been found earlier by Fuchs (205). The above diffusion theory applies equally well to the evaporation of aerosol droplets and its predictions were experimentally verified by Monchick & Reiss (206), who investigated the evaporation of droplets of diamyl sebacate down to a radius of 5×10^{-5} cm. in a Millikan oil-drop type apparatus. These authors also derived the evaporation rate from an appropriate solution of Boltzmann's equation of the kinetic theory of gases. The growth of an aerosol moving relative to the suspension medium at low Reynolds number [*Re*] of flow has been investigated by Frisch (207), the results being given as a power series in the [*Re*], and the rate of growth being affected only by terms of the order of $[Re]^2$ in agreement with the surmise of Fuchs (205). A treatment of diffusion-controlled aerosol growth in a turbulent medium has also been presented by Frisch (208). The influence of electrification and foreign vapors on the aggregation of aerosol particles has been studied by Dalla Valle *et al.* (209) who found that electrification had little effect on the rate of aggregation but a decided influence on the shapes of the aggregates. Substances which lower the vapor pressure of the suspended aerosol increase the rate of aggregation by removal of the "vapor cushion" surrounding a particle.

Behavior of aerosols in electrical fields.—The electrical properties of aerosols have been recently intensively investigated in view of possible applications to size studies and filtration of aerosols. The theory of the distortion of aerosol droplets by static parallel electric fields has been presented by O'-Konski & Thacher (210) who find that the droplet becomes longer in the direction of the field whether its dielectric constant is greater or less than that of the surrounding medium. The order of magnitude of this effect is small, e.g., a field of 30,000 volts per cm. causes a fractional elongation of 1 per cent in a cloud droplet which initially possessed a radius of 10μ. The authors predict an electrical birefringence in aerosols analogous to the Kerr effect, and suggest that their theory provides the basis for a novel method of measurement of sizes and the dynamic surface tension of aerosols. A new rapid method of measuring aerosol electrification by utilizing lateral deflection of an aerosol stream in an electric field has been developed by Hinkle, Orr & Dalla Valle (211). The filtration behavior of monodisperse electrically charged aerosols has been investigated by Goyer, Gruen and La Mer (212).

Determination of particle size and size distribution of aerosols.—A forward angle light scattering camera for determining size distributions in aerosols has been described by Lee & La Mer (213) applicable to particle radii in the range from 0.12 to 0.5 μ radius. Davies (214) has presented a review of recent work on light scattering and light absorption by particles based on Mie

theory while further tabulations of Mie scattering functions have been compiled by Gucker & Cohn (215) and Heller & Pangonis (216). Light scattering as applied to measure the polydispersity of dust clouds has been reported by Ellison (217), but is limited to cases where the size distribution is narrow in view of the dominance of scattering by the larger particles. Naik (218) has correlated optical ("Mie" light-scattering theory) and dynamic (sedimentation) methods of measuring the sizes of water drops in clouds and concluded that the values obtained from Mie theory are generally valid and lower than those obtained from the dynamic method. A number of new automatic counting and sizing devices have been reported which are of particular applicability to the study of aerosols (219, 220, 221) while a survey of work in this field has been presented by Walton (222).

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ISOTOPES[1]

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Introduction

The study of isotope effects has become a field in its own right and this review is restricted to papers on the physical chemistry of isotopic differences. Papers on radioactivity, age determinations, alteration of natural abundances by radioactive decay and fission, and tracer applications, have generally been omitted.

The emphasis of this survey has been directed toward a critical review and evaluation of the current status of work in geochemistry and chemical kinetics, reflecting the major interests of the reviewers. Isotope effects in chemical and phase equilibria have also been covered; more specialized topics such as nuclear masses and isotope separation have been omitted for the sake of adequate coverage of these four subjects.

The general subject of mass spectroscopy is dealt with in several recent contributions. Dibeler (1) lists 343 papers on all applications of mass spectroscopy, with a short comment on each. *A Handbook on Mass Spectroscopy* by Inghram & Hayden (144) is a concise and detailed discussion of the design and operation of ionic mass spectroscopes, with the emphasis on focusing characteristics of various mass analyzers; the discussion of ion sources includes a useful tabulation of the elements with the chemical compounds used in analysis by gas, crucible, and surface ionization sources, and the ions measured in the preferred method. *Mass Spectrometry*, by Robertson (145), is devoted principally to the phenomena of ionization and dissociation of molecules by electron bombardment, and to chemical analysis and investigations of free radicals. *Modern Mass Spectrometry* by Barnard (146) is the most extensive work on the subject available in English. It deals with all phases of mass spectroscopic work in detail and includes more than 500 literature references.

Relative Abundances and Isotopic Geochemistry

The year 1954 marked the appearance of two books devoted to geological effects of nuclear processes, and the proceedings of a national conference on this subject. These publications, the first of their kind, testify to the rapid

[1] The survey of the literature pertaining to this review was concluded in December, 1954.

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growth of the fields of nuclear geochemistry and geophysics. In this section an attempt is made to present a brief critical appraisal of our present knowledge of isotopic variations produced by geochemical processes, limiting the discussion in the main to those variations caused by differences in the physicochemical properties of isotopes.

Nuclear Geology, edited by Faul (2), contains brief descriptions of counting techniques and mass spectroscopy, and review papers by 26 authors on the effects of radioactivity in geology and the distribution of radioactive and radiogenic isotopes. Natural fractionation effects on stable isotopes are not treated, though certain papers deal with relative abundance variations caused by nuclear processes. In 1953, a conference on Nuclear Processes in Geologic Settings, cosponsored by the University of Chicago, The National Research Council, and The National Science Foundation, was held at Williams Bay, Wisconsin. The proceedings of this conference, edited by Inghram, Aldrich & Wasserburg (3), include 23 short papers on original work and some of the discussion which followed each. The papers cover a wide range of radioactive and stable isotope work in the earth sciences and several are referred to below.

Isotope Geology, by Rankama (4), covers all phases of radioactive and stable isotope work in geology in detail and presents an extensive bibliography of well over 1000 references. It is the first full-length attempt to systematize the large mass of accumulated data in this field, and is, therefore, worthy of considerable attention. The first section (150 pp.) is devoted to the physics and chemistry of nuclides, analytical techniques, and general geological and cosmological principles; the treatment throughout is highly elementary and qualitative. (Partition functions, for example, are not even defined, and are simply mentioned as Q's, whose ratios may be used to obtain exchange equilibrium constants.) The major portion of the book covers the periodic table element by element, presenting, in 275 pages, the available data on natural nuclear effects on the isotopic composition of each. Isotopic data on carbon, oxygen, sulfur, and hydrogen account for 40 per cent of this material, with relative percentages in that order. The presentation consists of a rather mechanical assembly of abstracts with little attempt at critical evaluation and synthesis of data or ideas. Where the author does inject his own discussion, there are many incorrect interpretations; a few examples bearing directly on the subject matter below may be given. Rankama states (p. 190) that the C^{13} content of atmospheric carbon dioxide is constantly decreasing due to preferential removal of C^{13} from the oceans by limestone; in actual fact, the mean carbon removed by the sediments is depleted in C^{13} with respect to the atmosphere, (see below) and, moreover, any trend in the mean surface composition must depend on a material balance including the carbon supplied to the system. Further, oxidation of light carbon in the biosphere obviously does not influence the atmospheric carbon isotope composition, as he maintains. The exchange equilibrium reaction for carbon between carbonate ion and carbon dioxide is discussed in

three places and written incorrectly twice (pp. 207, 209); the incorrect statements have evidently been taken directly from a paper by Urey without recognition of the fact that mole numbers for oxygen exchange had inadvertently been assigned to the compounds. Rankama states (p. 207) that agreement of the "calculated" value for this exchange equilibrium constant with the observed natural enrichment factor (numerically incorrect as given), also deduced by Landergren (p. 209), indicates precipitation of limestone under equilibrium conditions; both writers have failed to realize that the "calculated" fractionation factor was actually derived from the empirical natural abundance measurements. He believes (p. 221) that limestone loses C^{13} and C^{14} on exposure to the atmosphere, by exchange with carbon dioxide. Graphite, calcite, dolomite, and siderite are listed as "igneous" minerals (p. 193) and used to outline the range of "igneous carbon." HDO and H_2O^{18} are stated (p. 244) to have higher vapor pressures than ordinary water. Many explanations and discussions derived from the literature, obviously incorrect on the basis of present knowledge, are presented with no indication of doubt. The critical reader will, however, find the work very valuable for the comprehensive bibliography, which represents a real and badly needed contribution at this stage of growth.

Marble (5) continues to issue yearly reports on all phases of nuclear work in geology, in his capacity as Chairman of the National Research Council Committee on the Measurement of Geologic Time; recent issues include compilations of work on stable isotope variations. The bibliographies are extensive and thoroughly well-done, much miscellaneous unpublished material of interest is included, and the yearly summary report provides a well-integrated survey of current research.

Hydrogen.—Boato (6, 7) has determined the amount of water and the isotopic composition of the hydrogen in eleven carbonaceous chondrites, in an attempt to establish the primeval cosmic abundance of deuterium. There are twenty known meteorites of this type, all observed to fall; they are unique in containing up to 12 per cent of water and small amounts of organic compounds. The isotopic composition of the hydrogen is strikingly similar to that in terrestrial water; most of the stones yield water falling in the range of fresh waters, but four stones showed D concentrations ranging from 5 to 30 per cent higher than that of ocean water, definitely outside the range of terrestrial surface waters. The isotopic composition is thus different enough to establish the water as nonterrestrial, but shows that the meteoritic deuterium abundance is essentially the same as the terrestrial abundance (D/H of about 1/6500) and quite different from that of the sun (D/H less than 2.5×10^{-8}). Interpreted in the light of modern theories on the genesis of meteorites, these data indicate that the terrestrial and meteoritic figure is close to the true cosmic abundance of deuterium, and that deuterium has been consumed by nuclear reactions in the sun after the differentiation of planetary and solar matter, rather than having been highly enriched on the earth by some escape process.

Clarke, Denton & Reynolds (8) have made a precise mass spectrometric determination of the deuterium concentration in Thames River water, obtaining a value of 0.0152 mole per cent D. The general pattern of deuterium distribution in ocean waters has been accurately outlined by the mass spectrometric work of Friedman (9); the D concentration varies by about 2 per cent in open ocean waters not excessively affected by influx of fresh water. Friedman also reported data on some 34 fresh waters whose D concentration was found to range from about 0.6 to 15 per cent less than that of average ocean water. More recent determinations by Craig (unpublished) have indicated that some of Friedman's samples had been affected by extensive evaporation in faulty containers, and that the values listed for the Platte, St. Lawrence, Susquehanna, Apalachicola, Sacramento, San Joaquin, Red (of the North), and Snake Rivers should be discarded on this account.

The deuterium concentration in natural waters varies by 25 per cent, with surface fresh waters generally showing a depletion of 0 to 20 per cent in D compared with average ocean water (9, 10, 11). These meteoric waters are precipitated from the atmosphere in isotopic equilibrium with water vapor depleted in deuterium to varying degrees by multiple-stage fractional distillation processes, and are thus uniquely "labelled" as meteoric by the roughly constant ratio of D enrichment to O^{18} enrichment, both taken with respect to average ocean water. The present writers have studied the relationships between volcanic and hot spring waters and local meteoric waters by utilizing "natural" isotopic tracer techniques based on comparison of the D and O^{18} content of volcanic waters from areas of widely different surface water compositions (3, 10, 11). The heaviest natural water encountered occurs in a New Zealand volcano and has 3 per cent more deuterium than average ocean water. Many thermal waters show considerable enrichment in both isotopes, but the isotopic enrichment is due to evaporation of surface waters under nonequilibrium conditions, and the acid hot springs of volcanic areas appear to be of direct meteoric origin rather than representing condensed magmatic steam as postulated by current geological theory. In fact, it has been found both experimentally and from natural data that evaporation of water normally takes place under nonequilibrium conditions, such that kinetic, rather than equilibrium, factors govern the isotopic enrichment; thus waters such as Great Salt Lake show considerable excess enrichment in O^{18} over the concentration of this isotope in meteoric waters of equivalent D concentration, and fall distinctly off of a plot of D versus O^{18} concentrations in unevaporated meteoric waters. This discovery makes possible the immediate identification of evaporated waters and offers considerable promise for application to meteorology and hydrology. It is, however, apparent that for isotopic studies of water from sources other than direct meteoric origin, analysis of deuterium or oxygen 18 content alone will not yield any information about the origin of the water, and the concentration of both isotopes must be determined. Most of the literature on natural variations in the isotopic composition of water consists of work based on density determina-

tions which are often inconsistent and conflicting, and should be generally discarded. This includes all of the literature on hot spring and volcanic waters based on determination of one isotope alone or on total density. Much of this latter work is characterized by untenable conclusions, and there is so far no isotopic evidence to prove that any thermal waters are not entirely of meteoric origin, though of course such evidence may ultimately be found.

Suess (12) has recently confirmed the finding of Harteck & Suess (13) that the isotopic composition of atmospheric molecular hydrogen is the same as that of hydrogen in surface waters. This result indicates that the hydrogen is produced by photochemical decomposition of water vapor, since hydrogen derived from anaerobic decay of organic material is observed to be depleted in D via the exchange equilibrium between hydrogen and water. Hydrogen has escaped from the earth during geologic time in an amount roughly equivalent to the amount of free oxygen in the atmosphere plus the oxygen required to oxidize the necessary amount of ferrous to ferric iron in the crust of the earth; thus, as Harteck & Suess (13) observed, juvenile hydrogen should contain a smaller concentration of deuterium than the present ocean water. However, so little hydrogen has escaped relative to that in the oceans (12) that even if no deuterium escapes the earth's gravitational field, the effect is insignificant. Thus, juvenile hydrogen should have about the same isotopic composition as ocean water, unless the earth's interior originally incorporated hydrogen isotopically different from an amount of hydrogen which was concentrated at the earth's surface and was significant in amount compared to the quantity now in the oceans. The important remaining problem for understanding the isotopic geochemistry of hydrogen is, therefore, the determination of the isotopic composition of hydrogen in igneous rocks in all its various forms.

The occurrence of natural tritium was first demonstrated by Faltings & Harteck (14) who determined its concentration in atmospheric hydrogen. Suess (12) reported a new determination which showed, on the basis of Libby's data for natural waters, that the tritium concentration in atmospheric hydrogen is a thousand times higher than its concentration in rain water, and this result has recently been reconfirmed (15). However, the ratio of HTO to HT in nature is 1000 to 1, a phenomenon which has now been explained in detail by Harteck (16) in an incisive and comprehensive treatment of the kinetics of the various reactions involved. Korff (17) has briefly discussed the production of tritium and other cosmic ray-produced isotopes. The detailed assay of the distribution of tritium in natural waters has been measured by Kaufman & Libby (18, 19, 20) who find contents ranging between 0.5 and 67 tritium atoms per 10^{18} hydrogen atoms, with a production rate corresponding to a world inventory of some 1800 gm. Von Buttlar & Libby (21) have further extended the assay and determined the tritium production rate to be about 0.14 atoms per cm.^{2} per second. They have also applied the method to the dating of waters, and have found that certain thermal waters from The Geysers and Lassen Park, California, and Steamboat

Springs, Nevada, shown by Craig, Boato & White (10, 11) to be almost entirely of meteoric origin on the basis of D and O^{18} determinations, have the tritium content of modern rainwater. Fireman & Schwarzer (22) report tritium data obtained by measurement with a diffusion cloud chamber.

Lithium.—Baldock & Patton (23) reviewed the work on lithium natural abundance ratios up to 1951 and concluded that there was no satisfactory explanation for the wide spread of the data and the fairly consistent difference between the mass spectrometric and optical spectroscopic results. Hutchison (24) has now calculated the natural abundance ratio by an ingenious method independent of the analytical difficulties involved in previous determinations. Using the relationship between molecular weights, densities, and x-ray grating spaces for crystals, he obtained an expression for the atom fraction of Li^6 in terms of the atomic masses of the lithium isotopes and of fluorine, and a constant parameter dependent on molecular weight, density, and x-ray data which was evaluated for calcite, diamond, sodium chloride, and potassium chloride, averaged, and ratioed against the same function determined from data on a highly purified sample of LiF. The atomic mass of fluorine is accurately known from nuclear reaction data, and thus a value was obtained for the ratio Li^7/Li^6 of 11.53 which is believed to be correct to ± 0.29. This value disagrees with the bulk of previous data and Hutchison concluded that the mass spectrometric data are probably in error. (Equation 3 in this paper, the expression used in the calculation, is incorrect as given).

Cameron (3, 25) has studied the natural abundance ratio mass spectrometrically in an extremely painstaking investigation which would appear to be definitive. Using the Li_2I^+ ions obtained from sublimation of lithium iodide, he found that the isotope ratio thus obtained was independent of the ratio of Li_2I^+ to LiI^+ ions in the vapor, and that Li_2I^+ is probably the parent ion. Dissociation of the molecule with removal of a lithium introduced a measurable isotope effect. The high molecular weight precludes isotopic discrimination during sublimation, and the chemical preparation was such as to eliminate the possibility of a nonvolatile lithium compound in the iodide.

Cameron analyzed 19 samples of ore minerals, evaporite minerals, and commercial carbonates, and found a total variation in the ratio Li^7/Li^6 of 4 per cent, the range being 12.44 to 12.93. The silicate ore minerals (7 lepidolites and 4 spodumenes from different localities) showed a 2 per cent variation, 12.47 to 12.72, the ranges and averages for the two minerals being about the same, and this is the range assigned to the natural variation of the lithium isotope ratio. Other samples scattered over the total range and were excluded from consideration. With respect to commercial and evaporite samples, experiments showed that incomplete precipitation of carbonate and phosphate from solution produced an enrichment of Li^7 in the solid phase.

Kaplan & Wilzbach (147) have measured the lithium isotope ratio by thermal neutron activation. They irradiated a sample of commercial lithium carbonate and a standard made up from the separated isotopes, measured the tritium produced in the reaction $Li^6(n, \alpha)H^3$, and obtained a value for

the ratio Li^7/Li^6 in the sample of 12.35, in reasonable agreement with Cameron's data. Brody, Fred & Tomkins (148) obtained a ratio of 13.5 ± 0.2 in a series of optical spectrographic measurements on commercial salts, checked against mixtures of the separated isotopes. Their value falls much closer to the mass spectrometric data than do previous optical measurements, which cluster around a ratio of 8. Although the discrepancy between mass and optical spectroscopic data is thus not completely resolved, the indications are that Cameron's data are probably the most reliable at the present time. Hutchison's x-ray data are known to be internally consistent but may well be affected by systematic errors.

Carbon.—The understanding of the inorganic and biological carbon cycles and their interrelationships through geologic time is of fundamental importance for geochemistry, and a great deal of work has been done on the isotopic geochemistry of this element since the first investigations of Nier and his co-workers. In conjunction with the work on deuterium discussed above, Boato has investigated the isotopic composition of carbon in carbonaceous and ordinary chondritic meteorites (3, 7). The C^{13}/C^{12} ratio varies by 2 per cent with all values falling in the range of terrestrial material. The C^{13}/C^{12} ratio in ordinary chondritic meteorites is the same as in terrestrial igneous rocks, i.e., 2.5 per cent lower than the ratio in limestone, while the carbonaceous meteorites, which contain up to 3 per cent carbon, span the range between limestone and igneous rock carbon. These objects have evidently had an extremely complicated history which may be reflected in the above data; however, it appears that there is no evidence for such volatile elements as carbon and hydrogen having undergone any large scale isotopic fractionation during the processes by which terrestrial and meteoritic matter were originally accumulated.

The pattern of isotopic separation in the geochemical cycle of carbon is steadily becoming better understood and may be outlined briefly from the most recent study (26) in terms of enrichment or depletion in C^{13} with respect to average limestone as a base level. The C^{13}/C^{12} ratio varies by some 4.5 per cent, with most material containing less C^{13} than limestone. Ocean bicarbonate and atmospheric carbon dioxide contain respectively 0.2 per cent (27) and 0.7 per cent less C^{13} than average limestone, and the weighted mean of the active exchange reservoir is taken as -0.3 per cent on this basis; this mean includes the biosphere carbon consisting mainly of terrestrial and marine plants containing, on the average, 2.5 and 1.3 per cent less C^{13}, respectively, than limestone carbon. Carbon is continually removed from the reservoir by incorporation into marine sediments, and isotope effects occur in the depositional processes; thus, limestone carbon becomes slightly enriched in C^{13}, and the reduced carbon concentrated in shales is depleted in C^{13} to the extent of about 3 per cent with respect to limestone. The mean carbon deposited in the marine sediments during the course of geologic time, obtained from the weighted average of limestone and shale carbon, has about 1.2 per cent less C^{13} than average limestone, and thus the overall process of

transfer of carbon from the exchange reservoir to the sedimentary rocks is characterized by a 0.9 per cent depletion in C^{13}, if a steady-state situation is assumed.

The continual removal of carbon from the surface exchange reservoir requires that carbon continually be fed into the system, either as "juvenile" carbon from the earth's interior, or as "recycled" carbon released from buried sediments. Thus, the isotopic composition of the carbon supplied to the earth's surface over geologic time is intimately related to the fundamental problems of the origin of the earth and the rate and mechanism of transfer of material from the interior to the surface during the differentiation processes which have produced the present crust of the earth. A steady-state situation of constant isotopic composition of the surface exchange reservoir would demand that the carbon entering the reservoir also be 1.2 per cent depleted in C^{13} with respect to limestone carbon, and the evaluation of this point depends on many complex factors. The evidence derived from coal and shale indicates that isotopic constancy of the reservoir has been maintained for the last 10^9 years or so (26, 28). However, the igneous rocks and diamonds contain carbon depleted in C^{13} with respect to limestone by 2.5 and 0.3 per cent, respectively; neither figure matches the 1.2 per cent depletion in mean sedimentary carbon, and meteoritic carbon varies over this entire range, though the carbon in ordinary chondrites matches that in igneous rocks. It is clear that extensive research on the carbon supplied to the earth's surface at present and during the past must be carried out before the geochemical cycle of carbon can be understood; such work is now in process and some details have been reported. Craig has reported that the carbon emerging at Yellowstone Park has the isotopic composition of limestone (26), while that at The Geysers, California, has the composition of the mean sedimentary carbon (3, 10), with carbon from several other thermal areas falling in between. Naughton & Terada (29) find that carbon dioxide from the Sulfur Bank fumarole at Kilauea has the isotopic composition of limestone, while samples of carbon dioxide obtained from hot lava and evolved from the cold rock heated in vacuum fall in the range of carbon obtained by Craig by oxidation of Hawaiian basalts and other igneous rocks (26). Craig (30) analyzed the rings of a Sequoia tree and found that the isotopic composition of atmospheric carbon was constant to at least 0.1 per cent during the 2500-year interval from 900 B.C. to 1600 A.D., with a change in mean composition probably less than 0.02 per cent.

Rankama (31, 32) has vigorously reaffirmed his support of the argument, first proposed by Wickman (33), that the isotopic composition of graphitic carbon furnishes proof of its origin from limestone or from organic material. He defends his previous conclusion (34) that the carbonaceous accumulations known as *Corycium*, occurring in Archean slates and found to have an isotopic composition in the range of terrestrial plant and marine shale carbon, are the oldest certain vestiges of life, and further applies the argument to the deduction of an organic origin for some new Pre-Cambrian carbonaceous

material (35, 36). The reasoning involved in these studies has been criticized by Craig (28) in a detailed appraisal of the geochemical implications of data on the isotopic composition of carbon in ancient rocks. The assumptions involved in deducing the origin of carbon from isotopic data were found to represent unsolved problems in the geochemisty of carbon and to be unjustifiable *a priori*; it was concluded that on several different grounds the isotopic method of identification is not valid for such material, and the whole problem was reformulated in terms of basic geological and chemical concepts. Landergren (71) presents some 200 new analyses of the C^{13}/C^{12} ratio in carbon and carbonate in marine sediments. Carbonates in shales tended to contain less C^{13} than limestone, indicating some interchange with CO_2 of organic origin; his deduction that limestone carbon is precipitated in isotopic equilibrium was mentioned in the discussion of Rankama's book.

The pattern of carbon isotope variations in plants is well established from the data of Wickman (37) and Craig (26), which are in good agreement. The terrestrial plants generally contain from 2 to 3 per cent less C^{13} than average limestone, though a few anomalous specimens are heavier, containing some 1 per cent less C^{13} than limestone. Marine plants contain about 1.3 per cent less C^{13} than limestone. Wickman (37) explained the observed fractionation effects by a "cyclical enrichment process" operating in areas of normal terrestrial plant growth, in which the plants assimilate light carbon produced locally by respiration. The few anomalously heavy terrestrial plants and the marine plants were taken as representing growth in areas where a local system could not develop because of mixing by high winds or ocean currents; thus, these plants were believed to exhibit the true fractionation factor, which became compounded in the cyclical processes more generally operative. This problem of the mechanism by which plants fractionate the carbon isotopes has been studied in detail by Craig (27), who pointed out that Wickman's cyclical process violates the material balance requirements of such systems and that no cyclical mechanism can operate to produce an enrichment in the plants greater than that performed by the plants themselves. Craig's data showed that many plants growing in areas of high wind and sparse vegetation are as depleted in C^{13} as the plants in the biotopes most favorable for cyclic processes. The actual observed correlative factor was the association of the marine and anomalously heavy terrestrial plants with a carbonate phase containing carbon enriched in C^{13} with respect to atmospheric carbon dioxide. The normal factor by which C^{12} is enriched in terrestrial plants with respect to atmospheric carbon dioxide is thus $1.018 \pm .005$ where the indicated uncertainty represents the range in composition of the plants.

The steady-state fractionation factor obtainable in diffusion of carbon dioxide through a stagnant film of air to a totally absorbing surface is only 1.004, and the isotopic data thus indicate that gaseous diffusion is not rate-controlling in photosynthesis (27). CO_2 absorbed from air in $Ba(OH)_2$ is enriched in C^{12} by a factor of 1.015 (26). Baertschi (38) finds 1.014 for absorp-

tion from air, and a factor of 1.011 for absorption of pure CO_2 by NaOH. He concludes that his absorption velocity data conclusively rule out gaseous diffusion as rate-controlling in these experiments, and that the similarity of the observed factors with the square root of the mass ratio for CO_2 (1.011) shows that the fractionation is caused by the relative classical collision frequencies of the gaseous molecules with the liquid surface. These two conclusions, however, appear to be self-contradictory, and in the inorganic processes also, the disagreement of the observed factors with the diffusional factor of 1.004 indicates that the rate-controlling step is either the rate of diffusion of the reactants in the liquid or the chemical reaction rate itself, a conclusion in agreement with the great amount of data obtained for such processes by ordinary methods. Craig's considerations of the assimilation process in plants (27) indicated that the isotopic fractionation is produced in several stages, the first being the small relative solubility effect. This factor will be compounded with an equilibrium stage factor plus the first photochemical reduction step if the carboxylation process is markedly reversible, or with the first rate process after the last equilibrium reservoir of accumulated carbon, i.e., diffusion in the liquid or irreversible carboxylation. Additional fractionation will result from any other stage in which dismutation of a carbon carrier and fractional feedback occur. Finally, fractionation in the respiratory process can occur for plants not in the steady-state; the possible value of this factor was calculated roughly on the basis of the available data on the ratio of the fraction of assimilated carbon retained to the fraction respired and found to be too small to account for the overall fractionation factor characteristic of plants, but possibly significant. Baertschi (39) finds that CO_2 respired by beans sprouting in the dark has the same isotopic composition as the seedlings themselves, and considers that this observation will also hold for plants operating on the photosynthetic cycle. It is difficult to justify such an extrapolation, and, in fact, his experimental data on photosynthesizing seedlings show that the respired CO_2 is enriched in C^{13} by some 0.5 per cent with respect to the total assimilated carbon, the enrichment being in the same direction as that postulated (27) as a possible explanation of the observed maximum C^{13} depletion in tropical plants where the relative respiratory rate is at a maximum. The absence of a respiratory effect in Baertschi's experiments would require that a large fraction of the original seedling carbon be respired away after removal of the cotyledons, which appears doubtful; however the seedlings changed considerably in isotopic composition during the experiments and it appears that the experimental data cannot be regarded as definitive. Baertschi's experimental fractionation factor between plants and CO_2 is 1.026, somewhat higher than the largest factor yet observed for natural plants; however, all such factors observed in the laboratory have been higher than the natural factor and the data probably reflect some factor inherent in the experimental conditions which does not operate in nature.

The isotopic geochemistry of carbon 14 is of great interest not only for

dating but because of its application to problems concerning rates of mixing and transfer; in this case one is actually concerned with the problem of the nonoccurrence of an expected isotope effect. An important current development in carbon 14 work is the development of the acetylene counting technique by Suess (40, 41), by which ages up to almost 40,000 years can be determined on 1 gm. of carbon. Suess finds that modern marine shells have the same C^{14} activity as modern wood within ± 1 per cent; this result was indicated previously by the less precise data of Blau, Deevey & Gross (42) and has further been confirmed by de Vries & Barendsen (43). The implications of this unexpected finding have been discussed in terms of the data on C^{13} (27) which predict a 5 per cent enrichment of C^{14} in carbonates with respect to terrestrial plants, taking the isotopic enrichment ratio as 2. The determination of Van Norman & Brown (44) of a ratio of about 4.7 in photosynthetic assimilation is considered to reflect errors in correction factors applied to the assimilated incremental isotopic fractions (27) and the ratio of 2.4 obtained by Buchanan, Nakao & Edwards (45) is certainly more precise. Craig (27) studied the C^{13} and O^{18} content of a series of marine shells whose C^{14} activity had been measured and showed that the low C^{14} activity could not be ascribed to metabolic activity favoring the deposition of C^{12} in the shells, but must reflect directly the activity of the modern ocean bicarbonate. The conclusion was thus reached that the bicarbonate in the surface waters of the ocean has a radiocarbon age of 400 years, corresponding to the 5 per cent deficiency, which must be the result of slow transfer of carbon across the atmosphere-ocean interface. A slow mixing rate in the ocean itself will cause the deep waters to contain still less radiocarbon. Suess (3) reports data indicating that 19th century trees contained 3.4 per cent more radiocarbon when they grew than modern trees now contain, reflecting the percentage of dead carbon dioxide in the present atmosphere produced from the combustion of coal; thus the ocean bicarbonate is even older than 400 years because the isotope effect was applied to modern wood. The mechanisms and rates of the mixing of carbon through the phases of its geochemical cycle involve many complex factors and more precise isotopic data should be of great importance in their evaluation.

The understanding of the mechanism of isotopic fractionation by plants is of importance for radiocarbon studies; the "cyclical enrichment" process discussed above would cause only minor variations in the C^{14} content of plants while the effect of dilution with carbon from dead limestone can be very large, and thus the conclusion that the latter process is the actual cause of the anomalous C^{13} enrichments in some plants indicates the need for care in application of the dating method to fossil soils and low growing plants. The application of C^{13} determinations to various problems of this type and the relationships between C^{13} and C^{14} in natural processes have been discussed (27). The evaluation of the C^{13} enrichment which would be associated with C^{14} enrichment in fossil wood samples from preferential removal of C^{12} in postdepositional alteration, and C^{13} determinations on 16 samples of fossil wood ranging

in radiocarbon age from 2300 to more than 25,000 years plus several samples of decayed modern wood, showed that no significant C^{14} enrichment results from such a process. Deevey and his co-workers (46) have shown that plants growing in hard-water lakes can take up carbon of decreased specific activity, reflecting the slow rate of isotopic exchange between dissolved bicarbonate and atmospheric CO_2. Kulp (47) has briefly summarized the papers presented at the Conference on Radiocarbon Dating held at Andover, Mass., in 1954, and Libby (20) reviews the present status of C^{14} work.

Oxygen.—Dole and co-workers find that the O^{18} concentration in air samples taken at ground level from world-wide localities is constant to ± 0.025 per cent (48). Oxygen from altitudes up to 51.6 km. shows no significant difference from ground-level oxygen after correction of data on samples taken above 87,000 feet for the isotope effect in chemisorption on metal surfaces of the steel cylinders used for sampling in rocket flights. Air dissolved in Pacific Ocean water at depths down to 2500 meters is enriched in O^{18}, the enrichment increasing as the percentage of oxygen in the dissolved air decreases; the data are interpreted as reflecting the net result of production of light oxygen in photosynthesis and preferential consumption of light oxygen in respiration, with a simple process factor for the latter effect of 0.991.

Ocean water contains about 2 per cent less O^{18} than atmospheric oxygen, a fact for which no explanation based on direct experimental evidence yet exists (48). The general distribution of O^{18} in ocean waters is well-known from the recent mass spectrometric data of Epstein & Mayeda (49). They analyzed 93 marine and 7 fresh water samples, and found that the O^{18} concentration varies by 0.3 per cent in normal marine waters unaffected by direct mixing with fresh water. There is no marked correlation of isotopic composition and salinity for such waters, but the fractional change in O^{18} concentration per unit of salinity is generally greater than expected for loss of fresh water by simple process equilibrium evaporation. This effect is readily explainable in terms of material balance if the water vapor in the atmosphere suffers partial condensation under Rayleigh conditions, so that the precipitation returned to the ocean surface is enriched in O^{18} with respect to the vapor phase; the net loss from the evaporating layer is then of fresh water depleted in O^{18} by more than a single stage. The effect could also be attributed to a kinetic evaporation fractionation factor greater than the equilibrium factor, as observed in the case of fresh waters (cf. deuterium discussion), and it would be difficult to be certain of the correct explanation on the basis of salinity-O^{18} data alone. However, Friedman's data (9) on the deuterium content of many of the same waters show that a single linear relationship exists between the D and O^{18} content of both fresh and marine waters, with a slope corresponding to the isotopic vapor pressure ratio at ordinary temperatures. Thus, the fresh waters have been derived from vapor which has attained isotopic equilibrium in the evaporation process, probably because the large surface area of the ocean spray, the great travel distance, and the higher humidity provide mechanisms for the equilibration which are

not effective in the case of fresh water bodies. The fractional change in O^{18} content per unit of salinity in evaporating ocean water should be less than expected for a single-stage process in latitudes further toward the poles than the point at which the poleward-moving vapor becomes more than two stages lighter than the surface water. However, this effect is cancelled by the excess of precipitation over evaporation in these latitudes and the mixing with very light water from melting ice. The study of Epstein & Mayeda points the way for a detailed analysis of the material balance across increments of ocean surface, relating the addition of precipitation and inflowing water to the loss by evaporation and outflow; such a study involving D, O^{18}, and salinity should be valuable for many problems.

The work of Epstein & Mayeda and Friedman, taken together, provides the first solid foundation for the concept of light meteoric waters precipitating, under equilibrium conditions, from water vapor depleted in the heavy isotopes by multistage fractional distillation processes operating during the transfer of vapor from the oceans to the continents. O^{18} variations in marine and fresh waters have also been determined mass spectrometrically by Kirshenbaum and his co-workers (50), Baertschi (51), and most recently by Dansgaard (52, 53, 54) who reports analyses of 70 fresh waters ranging up to 3.2 per cent lighter than average ocean water. Dansgaard (54) presents a long series of equations designed to include all possible processes affecting the O^{18} concentration in fresh waters, and calculates a value for Copenhagen tap water which agrees with the measured value to within 0.02 per cent. Examination of the calculation, however, shows that it utilizes the measured value for the average O^{18} abundance in Copenhagen water vapor, found to be 2 theoretical plates lighter than ocean water, and that the introduction of this datum results in automatic cancellation of such variables as the single-stage evaporation factor, its variation with surface ocean temperatures, and an estimated factor for the presence of vapor derived from evaporation of fresh water. Thus, the calculation actually represents only the application of the empirical fractionation factor for liquid-vapor equilibrium to the measured vapor concentration, plus a small correction for the average amount of water precipitating during Danish storms which is actually the unknown which should have been calculated for comparison with an estimated value.

Isotopic variations in thermal waters and the kinetic fractionation observed in natural evaporation are mentioned in the section on deuterium. No new data on O^{18} variations in silicates have appeared since the work of Schwander (55) and Silverman (56). Silverman's data show that basic igneous rocks and stone meteorites are enriched in O^{18} some 0.7 per cent with respect to ocean water. Silicate and carbonate sediments are even higher in O^{18} concentration and thus erosion and sedimentation during geologic time have caused a continual depletion of O^{18} from ocean water whose overall magnitude is difficult to estimate. Exchange of surface waters with igneous rocks at high temperatures should cause the O^{18} concentration of the water to approach that of the rock, but should affect the deuterium content

only very slightly. Thus, on the assumption that the D/H ratio in ocean water is close to that of juvenile water (see deuterium section), juvenile water and recycled ocean water should be about the same isotopically in both D and O^{18} content and could not be easily distinguished. The problems involved in the isotopic geochemistry of carbon and water are very similar and their solutions rest fundamentally on an understanding of the material balance relations over all of geologic time.

Several new papers on the determination of paleotemperatures from the O^{18} variations in carbonate shells have appeared; the method, developed by Urey, Epstein and co-workers, depends on the temperature coefficient of O^{18} exchange between ocean water and marine shells, and has recently been described in detail (57). Lowenstam & Epstein (58) have made an extensive study of fossil material from the Upper Cretaceous period in an attempt to outline the potential applications of the method. They find evidence from different fossils and locations for a world-wide temperature maximum within the interval, and present a carefully detailed study of the limitations imposed by isotopic exchange during diagenesis. Determination of absolute temperatures is still not possible due to the uncertainty in the isotopic composition of the water, but with proper selection of material the evaluation of climatic trends during geologic periods appears feasible. Emiliani (59) presents data on O^{18} variations in benthonic Foraminifera in three deep-sea sediment cores from the equatorial Pacific, of Pliocene, Miocene, and Oligocene age. The evaluated results indicate a progressive temperature drop totaling 8°C. during the 30 million-year interval from the Upper Oligocene to the present, in good agreement with various geological estimates. The deep waters of open ocean basins should reflect the surface temperatures at the poles, and the uncertainty in the isotopic composition of such waters is believed to be small. Emiliani has also studied the depth habitats of pelagic foraminifera as indicated by data on O^{18} variations in different species and in the ocean waters in which they grew (60). His comparison of isotopically derived temperatures with the known oceanic temperature-depth relationships shows a definite depth stratification of different species in the surface waters as a result of limited tolerance for temperature and density variations.

Silicon.—Allenby (61) reports variations up to 1.4 per cent in the ratio Si^{28}/Si^{30}, in marked disagreement with data of Reynolds & Verhoogen (62), who find a range of only 0.3 per cent for similar material. The relative enrichments differ systematically by a factor of about 5. Thus, taking enrichments in the ratio Si^{30}/Si^{28} with respect to Yellowstone Park siliceous sinter, values for olivine-bearing lavas from Hawaii of +0.14 and +0.80 per cent are given by Reynolds & Verhoogen, and Allenby, respectively. Respective enrichments for diatomaceous earth from Santa Barbara, California, are given as +0.31 and +1.25. Both sets of data are internally consistent for groups of similar material, and both show the Yellowstone sinter as the lightest sample analyzed. Samples of pegmatitic quartz also yield values differing by a factor of 5, although in this case the samples are from different localities. Rankama

(4) reports unpublished data of Marsden which do not confirm either set of data; radiolarian and diatomaceous earths (including a sample analyzed by Allenby) are the lightest samples found, and silicon from lake water, silicified wood, and Archean quartz range up to more than 1 per cent heavier yet, thus doubling the range reported by Allenby. The systematic difference between the first two sets of data is much too great to be accounted for in any simple way and the explanation must await further work. Reynolds & Verhoogen converted their samples to $BaSiF_6$ by very careful wet chemical techniques and then removed SiF_4 for mass spectrometric analysis by thermal decomposition, recovering more than 95 per cent, and 90 per cent, of theoretical silicon yield in the two stages. Allenby treated his samples directly with HF in vacuum to obtain SiF_4 and reports no yield figures. Both sets of data were obtained on single collection mass spectrometers, utilizing, in the first case, magnetic scanning and a molecular leak; in the second case, manual accelerating voltage scanning and a capillary leak. Grant (63) presents a theoretical study of possible isotopic fractionation of silicon; he finds that in magmatic differentiation the heavy isotopes should concentrate in the late crystallizing silica-rich phases, with a maximum enrichment, with respect to the earliest phase, of 0.5 per cent, and that sedimentary silicon should be generally enriched in Si^{30} as is observed. Diffusion effects are calculated to be negligible.

Sulphur.—Thode and his associates have outlined the pattern of isotopic variation in the sulfur cycle in a remarkably thorough and systematic series of investigations, recently reviewed by Thode (64). The S^{32}/S^{34} ratio varies by some 7 per cent in nature, the sulfates generally being enriched, and the sulfides and organic sulfur being depleted, in the heavy isotopes. Meteoritic and igneous sulfides are intermediate in composition. Thode, Macnamara & Fleming (65) found that sedimentary sulfides and sulfates of recent origin differ in isotopic composition by 7 per cent, but samples of increasing geological age approach more and more closely the isotopic composition of sulfides in igneous rocks, and samples older than 700 million years show very little difference in composition. They interpret the results as indicating the establishment of thermodynamic equilibrium by the fluxing of sulfur through the biological sulfur cycle since this early time; the maximum difference between modern sulfates and sulfides is almost exactly the equilibrium distribution at 25°C. between SO_4^{--} and H_2S. Thode, Wanless & Wallouch (66) have studied the origin of sulfur in Texas and Louisiana salt domes, in which the native sulfur is generally assumed to have been formed from the associated calcium sulfate by reduction either with organic matter or through bacterial action. The native sulfur is enriched in S^{32} with respect to the sulfate by some 4 per cent, about the same factor as is observed in the sulfur-producing African lakes where the reduction process is observed to proceed through the agency of bacteria. Residual sulfate in contact with sulfur shows varying degrees of S^{34} enrichment indicating a "batch process" in an aqueous phase. In addition, it was found that carbon in the associated calcium carbonate is greatly depleted in C^{13}, ranging from some 3 to 5 per cent low in C^{13}

compared with average limestone; petroleum and other organic materials are 2 to 3 per cent lower in C^{13} than limestone (see carbon section), therefore the data indicate that carbon has most probably been derived from organic matter via a second fractionation step similar to that observed in decarboxylation reactions. This carbon is the lowest in C^{13} abundance yet found in natural materials. Altogether, the data furnish convincing evidence for production of sulfur and calcium carbonate by the action of sulfate-reducing bacteria operating on calcium sulfate and essentially burning oil for a free energy supply.

Other elements.—Dole and co-workers also found that nitrogen in Pacific Ocean water down to 2500 meters depth and in samples of air up to 51.6 km. in altitude has normal isotopic composition (48). Kerwin (67) reports that phosphorus is monoisotopic to better than one part in 50,000. Owen & Schaeffer (68) investigated chlorine in ten samples of natural material, including igneous rocks, scapolite and sodalite, salt from ocean water, Great Salt Lake, and a salt dome, and found no variation in isotopic composition. The precision was such that variations greater than 0.2 per cent of the ratio would have been observed; the lack of variation is attributed to the absence of oxidation-reduction processes in the general cycle of chlorine. They report a ratio Cl^{35}/Cl^{37} of $3.13 \pm .03$ for the average of the 10 samples, in good agreement with the value of 3.096 obtained by combining the data of Harkins and Stone with Nier's atomic masses. Hogg (69) reports that Nier's chlorine ratio of 3.07 used in equations for the mass spectra of $TiCl_3^+$ gives best agreement between calculated and observed titanium isotope abundances, with a deviation of ± 1 per cent giving large discrepancies. Hogg finds that titanium from samples of ilmenite and rutile from various types of deposits of different age is constant in isotopic composition to better than 1 per cent. Cameron (3, 70) analyzed five bromine samples from ocean water, Searles Lake, and Michigan and West Virginia Silurian salt deposits, and found no significant variation, as would be expected on geological grounds. He reports a value of $1.0217 \pm .0002$ for the ratio $NaBr^{79}/NaBr^{81}$, in agreement with the value $1.0210 \pm .0020$, obtained by Williams & Yuster on Br_2 vapor, and accepted by Bainbridge & Nier as the best value.

Conclusions.—The field of isotopic geochemistry is quite evidently in a state of vigorous growth. Much of the work is, of course, still in a stage of dependence, requiring interpretation and explanation in the light of geological, meteorological, and other evidence. Nevertheless, direct contributions to problems in the earth sciences have already been made; examples would include problems such as the origin of atmospheric hydrogen, diffusion as a rate-controlling process in photosynthesis, the genesis of sulfur in salt domes, temperatures of the oceans in past geologic periods, origin of thermal waters, etc. Such contributions will continue to be developed and it appears very likely that isotopic studies will prove to be as valuable in the earth sciences as they are in the field of chemical kinetics. There are various problems involved in the use and comparison of standards and in the methods of report-

ing analytical data. The practice used by Rankama in his book (4) of recalculating isotopic data, originally reported in relative enrichments, to absolute ratios, is particularly to be deplored; it involves a great deal of complicated juggling of absolute determinations, many of which are of questionable precision, and contributes nothing, since the values necessary for use in discussing isotopic problems are, in fact, the relative isotopic enrichments. Thus, to get the relative enrichments reported for carbon by Craig, hydrogen by Friedman, and oxygen by Silverman and Baertschi, from Rankama's book, one must undo all Rankama's calculations to recover the original figures. Most mass spectrometric data on relative abundances are currently obtained by some form of comparison with a standard, and it is difficult to see how the procedure, used by some workers, of choosing an absolute ratio for the standard and then converting all relative enrichments to absolute ratios on this basis, adds anything to the value of the data. What is necessary at this point is a set of international standards for the various elements so that all workers can report isotopic data in terms of enrichment relative to the same standards, and it is hoped that this problem will be resolved before long.

Isotope Effects in Chemical Equilibria

Friedman & Haar (72) have developed a procedure for machine computation of partition functions for nonrigid rotating anharmonic oscillators, including vibrational-rotational coupling terms and low temperature rotational corrections. They report values for the thermodynamic functions of the various protium-deuterium-tritium water molecules evaluated from 50° to 5000°K. on the National Bureau of Standards SEAC. The data on H_2O are in good agreement with those of the Ohio State group, obtained by direct summation of the unexpanded partition function, and with the results of the Gordon-Wagman *et al.* calculation which uses a partition function expansion similar to that developed for use on the SEAC. Kwart, Kuhn & Bannister (73) report equilibrium constants for the exchange reactions

$$CH_3OH + D_2O = CH_3OD + HDO \qquad K_1 = 2.00$$
$$CH_3OH + HDO = CH_3OD + H_2O \qquad K_2 = 0.50$$

obtained by direct infrared spectroscopic analysis in order to eliminate possible catalytic effects in the separation of the reaction components. Their values of 1.81 and 0.46 obtained at room temperature are close to the statistical values given above. They find a reaction half-life of less than 20 sec. in both liquid and gas phase exchange, and conclude that the reaction proceeds mainly through the agency of unshared pairs of oxygen. Bigeleisen & Kant (74) have studied the exchange reaction

$$HD\,(g) + UH_3\,(s) = H_2\,(g) + UH_3D\,(s)$$

for which the equilibrium constant varies from 2.04 to 1.34 in the temperature range from 195°K. to 433°K., and thus passes through a minimum before rising again to the statistical value of 1.50. This temperature dependence is explained on the basis of the vibrational frequency changes on substitu-

tion of D in UH_3 and the relative temperatures for equipartition distribution of frequencies in the isotopic uranium hydrides, and leads to an explanation of the temperature independence of the ratio of the dissociation pressures of UH_3 and UH_2D. The derived heat of reaction for

$$UH_3 + 3/2\,D_2 = UD_3 + 3/2\,H_2$$

is -641 ± 50 cal., in close agreement with the calorimetric value of Abraham & Flotow of -669 ± 45 cal.

Spindel (75) has calculated equilibrium constants for exchange of nitrogen between NO_3^-, NO_2, NO_2^-, and NO at 25°C. Use of the valence force field approximation for NO_2 yields a partition function ratio 2 per cent greater than that obtained with a central force field. Sheppard & Bourns (76) report equilibrium constants at 20°C. for S^{32}–S^{34} exchange between bisulfite ion and the bisulfite addition product of three aldehydes and five ketones, i.e.,

$$HS^{34}O_3^- + R_2\overset{\overset{OH}{|}}{C}S^{32}O_3^- = HS^{32}O_3^- + R_2\overset{\overset{OH}{|}}{C}S^{34}O_3^-$$

The values range from 1.021 for acetone to 1.010 for anisaldehyde and show a fairly regular decrease with increasing molecular weight of the carbonyl component. Equilibrium constants of this magnitude are expected if the addition products have a carbon-sulfur bond corresponding to a sulfonic acid salt structure and the bisulfite ion has only sulfur-oxygen bonds. If the addition products were α-hydroxysulfite ester salts with a carbon-oxygen-sulfur bond structure, the sulfur atom is always bound to three oxygen atoms and thus should give a much smaller exchange constant, unless the bisulfite ion contains a sulfur-hydrogen bond. Sheppard & Bourns find that there is no isotopic fractionation of sulfur between bisulfite ions and sulfite ions, indicating that sulfur is probably bound only to oxygen in the bisulfite ion, and that, in any case, the fractionation between bisulfite ion and a sulfite ester addition product, involving the same change in sulfur bonding, should be small. The large equilibrium constants thus support the sulfonic acid salt structure of the carbonyl-bisulfite addition compounds, in agreement with a wealth of chemical and physical evidence from other studies. Taube (77) has reviewed the work of his group on the use of oxygen isotope effects in the study of the hydration of ions, utilizing both kinetic methods and equilibrium studies. The bulk of the review is devoted to a discussion of the change in the O^{18}/O^{16} ratio in water as a function of salt concentration, due to establishment of isotopic equilibrium between "free" water and water which interacts with the salt.

Isotope Effects in Chemical Kinetics

Carbon isotopes.—In order to see if complete agreement can be reached between experimental data and the theory of isotope effects in reaction rates, more careful quantitative work has been done on the decarboxylation of malonic acid. Yankwich & Belford, who previously studied the C^{13} inter-

molecular effect of normal malonic acid in quinoline from 34° to 118°C. (78), have now measured the C^{13} intramolecular effect in the same medium and about the same range of temperatures (79). The intramolecular effect is measured by the ratio k_4/k_3 of the following reactions:

$$C^{13}O_2H \xrightarrow{k_3} C^{13}O_2 + C^{12}H_3C^{12}O_2H$$
$$C^{12}H_2$$
$$C^{13}O_2H \xrightarrow{k_4} C^{13}O_2 + C^{12}H_3C^{13}O_2H$$

If R_C, R_D, R_M are the ratios of the carbon isotopes in CO_2 after complete decarboxylation, malonic acid, and carbon atom in methylene position, respectively, then $k_4/k_3=(3\ R_D-R_M-R_C)/R_C$. R_M was measured to check the identity of isotopic composition of carbon atoms in positions 1, 2, and 3. The values of k_4/k_3 range from 1.0455 at 86°C. to 1.0317 at 138°C., thus indicating a marked temperature dependance which is not predicted by the Bigeleisen model for intramolecular effects.

The k_4/k_3 value at 138°C. is in good agreement with the value 1.0292 ± 0.0007 at 140°C. obtained in the decarboxylation of liquid malonic acid near the melting point in a subsequent study by Yankwich & Promislow (80). This latter ratio has been measured by many workers with somewhat scattered results; the value of Yankwich & Promislow should be definitive since many cross-checks were employed and the internal consistency of the results was good. Bigeleisen's theoretical value of k_4/k_3 is 1.0198 and is independent of temperature (81). While the k_4/k_3 values and temperature dependance in quinoline medium may be partly explained by some effect of the solvent, the disagreement for liquid malonic acid is yet to be understood. Yankwich & Belford give a tentative explanation based on a strengthening of one of the C–C bonds in the transition state while the other one is loosened.

A communication of Yankwich, Promislow & Nystrom (82) gives a definite answer to the long debated question of whether the intramolecular C^{14} effect in the decarboxylation of malonic acid can be more than twice the C^{13} effect. For details see the previous review articles by Thode (1953) and Jones (1954), and papers by Yankwich & Stivers (83), Bigeleisen (81), and Bigeleisen & Wolfsberg (84). Yankwich & Stivers had again found a C^{14} effect definitely greater than the expected value and more than three times larger than the C^{13} effect. C^{14} was measured by counting, C^{13} by mass spectrometry. Bigeleisen & Wolfsberg concluded that something was certainly wrong, because the data were internally inconsistent with other measurements on the intermolecular effect, which is necessarily correlated with the intramolecular one. From the experimental evidence available at that time, they were able to maintain that, notwithstanding Yankwich's results, the ratio of C^{14} to C^{13} isotope effects in malonic acid decarboxylation must be about two, in agreement with the theoretical value. This fact was finally acknowledged by Yankwich, Promislow & Nystrom (82). Using the same careful experimental technique employed in (80), and making the analyses

entirely by mass spectrometry on the same material, these authors report a k_4/k_3 ratio of 1.0545 ± 0.0046 for the C^{14} effect and of 1.0285 ± 0.0009 for the C^{13} effect in the decarboxylation of liquid malonic acid at 140.5°C. The ratio of the two effects is 1.91 ± 0.17, a figure in excellent agreement with the theoretical value. Using the authors' words, "these results indicate strongly that the malonic acid case can no longer be considered deviant from the predictions of the absolute rate theory," a conclusion that was strongly hoped for by all workers in this field of research.

Bigeleisen's theory on isotope effects has been compared by Bernstein (85) with the results obtained in a study, by a static method, of the C^{13} effect in the homogeneous thermal decomposition of nickel tetracarbonyl. The rate constants are defined as

$$Ni(CO)_4 \xrightarrow{k_1} Ni(CO)_3 + CO$$

$$Ni(CO)_3C^{13}O \xrightarrow{k_2} Ni(CO)_3 + C^{13}O$$

$$Ni(CO)_3C^{13}O \xrightarrow{k_3} Ni(CO)_2C^{13}O + CO$$

on the assumption that the rate-determining step of the decomposition is the rupture of a Ni–C bond, as is likely to be true. If R_{CO} and R_N are the C^{12}/C^{13} ratios in the first fraction of CO and in the nickel carbonyl, respectively, then, approximately, $R_{CO}/R_N = k_1/(k_2+k_3)$. On the hypothesis that the intramolecular effect, defined as $k_3/3k_2$, is the square root of the ratio of the Ni–C^{12}, Ni–C^{13} reduced masses, it is possible to calculate the intermolecular effect from the experimental data. In the temperature range 30° to 105°C. the intermolecular effect is found to be

$$k_1/4k_2 = 1.0481 - 6.7 \times 10^{-5}t(°C.)$$

Comparison of these data with a theoretical treatment made using the method of Bigeleisen is given, but the agreement is not completely satisfactory. Here also, as in the malonic acid case, the temperature dependence is not well reproduced by the theoretical model.

Ropp *et al.* (86) have tried to duplicate the results obtained in 1952 by Roe & Albenesius (87) for the iodoform reaction of acetone-1-C^{14}. A "reverse" isotope effect (C^{14}rate greater than C^{12}rate) had been reported by these latter authors but the new experiments failed to show such a phenomenon, and no measurable intra- or intermolecular effect was found. A small effect in the normal direction was also observed for the Schmidt reaction of acetone-1-C^{14}. Thus, there is, at present, no substantiated case for a reverse carbon isotope effect in reactions controlled by rate of bond rupture. Bigeleisen's treatment of isotopic reaction rates (88) indicates that the most favorable conditions for a reverse effect are those in which bond formation is rate-controlling. Stevens & Crowder (89) therefore investigated the condensation of benzoyl-benzoic acid to anthraquinone in concentrated sulfuric

acid, where Newman's study (90) had indicated a reaction mechanism consisting of two equilibrium stages followed by a benzene substitution in which the carbon to carbon bond formation could be the rate-controlling step. A reverse carbon isotope effect was indeed found, with $k^{14}/k^{12} = 1.074 \pm .003$. In Bigeleisen's formulation, a reverse effect indicates that the activated complex molecules are more tightly bound than the reactant molecules, and by a factor large enough to outweigh the reduced mass effect, which always favors the normal rate constant ratio. Stevens & Crowder consider that, in the reaction studied, the activated complex molecules are indeed more tightly bound because of the partial formation of a carbon-carbon bond with transformation of some internal rotational degrees of freedom in the reactants to bending vibrational modes in the activated state. The energy levels in the activated state are thus more widely spaced than in the initial state and the activation energy becomes greater for the lighter molecules. They conclude that bond formation must be rate-controlling and that Newman's mechanism is thus supported, though the magnitude of the isotope effect is admitted to be surprisingly high in view of the fact that the tendency toward a reverse effect is opposed by the reduced mass factor. Lee & Spinks (91) studied the synthesis of 3,3′methylene-bis-4-hydroxycoumarin in which bond formation might also produce an isotope effect. From Bigeleisen's equation, the ratio k^{12}/k^{14} should be at least less than 1.04, the reduced mass term, if bond formation is the rate-controlling step in the reaction. The observed ratio is 1.07, which is normal and is in reasonable agreement with the effect they predict for a rate-controlling step of slow dehydration, rather than bond formation. The authors, however, stress the qualitative nature of their conclusions. The effect of ring substituents on isotope effects has been studied by Ropp & Raaen (92), who investigated the saponification of ethyl benzoates (α-carbon-14) and the formation of the 2,4-dinitrophenylhydrazone of acetophenones (α-carbon-14). The same authors (93) studied a Meerwein reaction of butadiene-1-C^{14} and found no preference of the diazonium compound for reaction with a C^{14} or C^{13} end-carbon atom.

Attree *et al.* (94) report measurements on the relative reaction rates of $C^{12}O$, $C^{13}O$, and $C^{14}O$ with oxygen, all measured mass spectrometrically. The heterogeneous reaction gave $k_{13}/k_{12} = .984$ and $k_{14}/k_{12} = .959$ which agree with the relative classical collision frequencies with the walls, namely .983 and .966. No isotopic effects were found in the homogeneous reaction. Using the Bigeleisen-Wolfsberg formulation (95) in conjunction with a model for the chain propagating step which assumes an activated complex composed of CO and O_3 in linear alignment, with O_2 as a point mass, the authors found that a zero isotope effect is predicted for a wide range of potential constants, if the ratio of the transmission coefficients is unity.

Hydrogen isotopes.—Henderson & Bernstein (96) have made quantitative measurements on the deuterium isotope effect in the reaction of water vapor with zinc, a well-known effect to workers in the field of hydrogen isotopic measurements since the zinc reaction is the most common method of prepa-

ration of hydrogen samples for mass-spectrometric analysis. The effect was measured over the temperature range 295° to 415°C. The initial fractionation factor, that is the ratio of reaction rates, was established as 1.6 ± 0.1 at 400°C. A small temperature dependence is observable. The results are compared with the rough model of Eyring & Cagle (97) for the rupture of an isolated oxygen-hydrogen bond. The correction factor required for incomplete conversion of water to hydrogen by the zinc method at 400°C. is given graphically, and shows that more than 99 per cent conversion is necessary to obtain negligible fractionation.

A deuterium isotope effect is reported by Bryce-Smith, Gold & Satchell (98) in the metallation of benzene and toluene, where k_D/k_H, the ratio of the rates of displacement of D and H by a metal atom, was found to be 0.5 for the benzene, 0.2 for the toluene reaction. The aim of the work was to test the validity of protophilic mechanism for aromatic metallation. Kaplan (99) found a remarkable tritium isotope effect in the bromine oxidation of ethanol. The ratio of the rates of removal of tritium and hydrogen atoms from the methylene carbon, k_T/k_H, was found to be 0.15 ± 0.02 at 37.5°C., on the plausible hypothesis that CH_3–CH_2OH and CH_3–CHTOH are oxidized to the same extent to CH_3–CHO and CH_3–CTO, respectively. The result is concluded to rule out the formation of ethyl hypobromite as a precursor of acetaldehyde in the oxidation. Another case in which the hydrogen isotope effect has been of value in the study of an oxidation reaction is the work of Wiberg (100) on deuterium effects in the chromic acid oxidation, the Cannizzaro reaction, and the benzoin condensation of benzaldehyde. k_D/k_H was found to be 0.23 in the case of chromic acid oxidation, indicating cleavage of the C–H bond as the rate-determining step. A k_D/k_H value of 0.55 was found, however, for the Cannizzaro reaction, a value unusually low for an ionic reaction. Various possible explanations are considered. The thermal decomposition of chloroform and chloroform-*d* from 450° to 525°C. has been studied by Semeluk & Bernstein (101). The rate of decomposition of deuterated chloroform was found to be 20 per cent less than that of ordinary chloroform. This small isotope effect is considered to be strong evidence against a C–H bond dissociation in the primary step. Therefore, the reaction $CCl_3H \rightarrow CCl_2H + Cl$ is supposed to be the primary dissociation, followed by others until the end products, HCl, and tetrachloroethylene, are formed.

The homogeneous exchange reaction between hydrogen and deuterium in the gas phase has been re-examined by Boato *et al.* (102, 103). The reaction

$$H_2 + D_2 \rightleftharpoons 2HD$$

was investigated by Farkas & Farkas in 1935 (104), and more recently by Van Meersche (105), but the comparison with the theory of absolute reaction rates was not thoroughly satisfactory. The reaction is worth careful study because of the importance of a definite test of the transition state method in one of the simplest chemical reactions. The exchange proceeds through two steps: (*a*) formation of H and D atoms from the thermal decomposition of H_2 and D_2 at the walls; (*b*) exchange reactions

$$D + H_2 \xrightarrow{k_3} HD + H$$

$$H + D_2 \xrightarrow{k_4} HD + D$$

The reaction was studied in the temperature range from about 600° to 730°C. Good reproducibility was obtained only when air was prevented from diffusing into the quartz reaction vessel by enclosing the vessel in an evacuated quartz jacket. Air diffusion through the walls of the reaction vessel must have vitiated the previous experiments, since oxygen is found to catalyze strongly the exchange reaction through the formation of water. Heterogeneous contribution from the walls was found to be negligible. The experimental data show that the overall reaction rate is slower by a factor of 1.9 than that previously obtained by Farkas & Farkas and Van Meersche. With an improved kinetic treatment of the reaction, the ratio k_3/k_4 of the reaction rates of the atomic exchanges can be calculated directly, and is found to be 1.6 at 1000°K. The reaction order is 3/2 and the total activation energy is 60 ± 0.5 kcal., in complete agreement with the previous authors. Consequently, an activation energy of about 7.2 kcal. should be adopted for the reaction between atom and molecule. The validity of the transition state method was tested by a comparison of the given data and the low temperature data of Geib & Harteck, using the method of Farkas & Wigner (106); a remarkable improvement with respect to the Farkas data was obtained.

The influence of the substitution of deuterium for hydrogen in the β-position of alkyl halides and similar compounds has been studied in solvolytic reactions. Shiner (107) found that the solvolysis rate for 2,3-dimethyl-2-chlorobutane in 80 per cent aqueous alcohol is lowered and the activation energy is raised by 580 cal., if the tertiary hydrogen is replaced by deuterium. Lewis & Boozer (108) report that substitution of D for H in 1 and 3 position in 2-pentyl bromide and 2-pentyl toluenesulfonate slows down the solvolysis rates by a factor of 1.3 to 1.7. Boozer & Lewis (109) studied the decomposition of secondary alkyl chlorosulfites in dioxane and isooctane between 60° and 95°C. If the chlorosulfites are extensively deuterated in the 1 and 3 position, the decomposition proceeds at a slower rate. Finally, Lewis & Coppinger (110) give data for the acetolysis of methyl-*p*-tolylcarbonyl chloride. They compared the normal rate with the rates of the same solvolytic reactions when deuterium is substituted for hydrogen in one of the two methyl groups. It is found that the rate decreases in both cases, though to a minor extent in the case of the *para*-methyl groups. The result constitutes the first example of an isotope effect produced by isotopic substitution at a point so far removed from the seat of reaction. These isotope effects where the isotopic atoms are not involved in a bond rupture are difficult to explain quantitatively, but they represent a new method of attack for the solution of organic chemical problems.

Oxygen isotopes.—Hutchison (111) has studied the kinetics of oxygen exchange in the systems water-silica and oxygen-silica. No exchange between oxygen and silica was found up to 1000°C. Exchange between water and

silica containers was obtained at 960°C. with a reaction half-time of 47 min., while at 750°C. the half-time was 100 min. The experimental activation energy was determined as 4.6 kcal./mole deg., which is interpreted in terms of a predominate surface rate-controlling reaction. Some evidence was also found for a homogeneous phase reaction between water and dissolved silica at the higher temperature. Dole & Lane (112) measured the oxygen isotopic fractionation in the formation of oxide films on steel and copper. They found that O^{16} was chemisorbed preferentially on steel by a factor of 1.025 to 1.028, and on copper by factors ranging from 1.052 to 1.074, indicating significantly different effects for the two metals.

Other elements.—The work of Sheppard & Bourns (76) on the sulfur isotopic exchange equilibrium between bisulfite ion and the bisulfite-addition products of some aldehydes and ketones is described in the section on chemical equilibrium. Sheppard, Bader & Bourns (113) extended the work in a study of the relative rates of reaction of the sulfur isotopes in the forward reaction alone with heptanal, benzaldehyde, anisaldehyde, and 2-heptanone at 25°C. They found that with all reactants but benzaldehyde the reaction rates differed by no more than 0.2 per cent; for benzaldehyde a ratio k_{32}/k_{34} of 1.003 was obtained. They concluded that, expressed in terms of the Bigeleisen formulation, the rate-determining step is the formation of a carbon-sulfur bond, resulting in tighter binding of the atoms in the activated state, and thus giving a zero-point energy effect less than unity which just cancels the reduced mass effect (cf. the work of Stevens & Crowder on the reverse C^{14} effect, discussed above). Assuming an activated complex model in which the new bond is completely formed, they calculate a ratio k_{32}/k_{34} of 1.001. Bartholomew, Brown & Lounsbury (114) found a chlorine isotope effect of 1.008 in favor of Cl^{35} in the reaction of *tert*-butyl chloride with alcoholic silver nitrate and sodium hydroxide.

Phase Equilibria and Related Topics

In this section, work on He^3 and He^4 is not reviewed, and the reader is referred to the reviews on Cryogenics and Solutions of Nonelectrolytes. Cohen, Offerhaus and de Boer (115) have made a quantum mechanical calculation of the properties of gaseous mixtures of these isotopes and the equation of state. The general theory of isotopic mixtures in condensed phases has been subjected to detailed treatment in a series of papers by Prigogine *et al.* (116, 117, 118), and compared with experimental data on hydrogen and helium isotopic mixtures (119). Reference is made to Progogine's review on Statistical Mechanics for discussion of these papers.

Several interesting papers appeared dealing with the properties of liquid and solid hydrogen and deuterium. The low temperature research group at Ohio State studied the PVT properties of the liquids between the triple and the critical points and up to 100 atm. (120, 121). The isochores were found to be straight lines, terminating at the saturated vapor pressure curve. The

data are not in agreement with the Lennard-Jones and Devonshire equation of state for compressed fluids, and Hamann (122) points out that the discrepancy may be due in great part to quantum effects. Calculation of the corrections to be made to the Lennard-Jones and Devonshire isotherms resulted in satisfactory agreement with the experimental data. The melting temperatures of H_2 and D_2 as a function of pressure were measured by Chester & Dugdale (123) up to 2800 kg./cm.^{2}. The striking result was obtained that the pressure necessary to melt hydrogen at a given temperature is always higher by about 170 kg./cm.^{2} than that necessary to melt deuterium at the same temperature. This effect is probably connected with the influence of zero-point energy on the melting process, and such work may be useful in throwing light on the nature of this process. The effect of compression on solid H_2 and D_2 at liquid helium temperature has been studied up to 10,000 atm. by Stewart & Swenson (124). The solid H_2 and D_2 were found to be highly plastic and difficult to handle under pressure. Their molar volumes decrease by a factor of about two from 0 to 10,000 atm., and an extrapolation of the data, using an equation of Birch to fit the results, indicates that one must go to 180,000 atm. to obtain another factor of two. The differences between H_2 and D_2 are explained in terms of the zero-point energies.

The vapor pressures of light and heavy water have been redetermined by Combs, Googin & Smith (125, 126) with a precise gas saturation method in the temperature range from 10° to 55°C. Their values of D_2O vapor pressures are slightly lower than those given by Kirshenbaum (50). The density and viscosity of heavy water up to 250°C. and surface tension up to 216°C. have been measured by Heiks *et al.* (127); density determinations were made to the nearest 0.0003 gm./cc. The ratio of densities of D_2O to H_2O was found to increase slightly up to 80°C and then to decrease steadily, in agreement with previous indications. D_2O was found to be more viscous than H_2O by about 21 per cent at 30°C. and 9.7 per cent at 250°C. The temperature effect on viscosity is quite similar, indicating a similar degree of association. The surface tensions are about the same at 100°C., but with increasing temperature the surface tension of D_2O becomes progressively less than that of H_2O, the difference being about 3 per cent at 220°C.

Isberg & Lundberg (128) analyzed mass spectrometrically the O^{18} content of electrolytically enriched D_2O. They find an O^{18} enrichment of 10 per cent, much less than the value of 50 per cent reported by Tronstad & Brun (129) on the same kind of water. The value of Tronstad & Brun has been generally adopted for correction of the density measurements of heavy water, and thus all the D_2O density data presently available in the literature are incorrect by a factor of about 0.1 per cent. This error is large enough to affect remarkably the precise densitometric determination of the concentration of deuterium in heavy water. Another error in previous isotopic measurements on water was found by Watson (130) who remeasured the O^{18} effect on the refractive index by an interferometric method. The change in re-

fractive index at 18°C. (white light) for a molecular proportion y of H_2O^{18} was found to be 0.00008 y, the proportional factor being only one-tenth of the previously accepted value.

The vapor pressures of isotopic compounds are still under study and no satisfactory step toward the complete understanding of this subject appears to have been made. The vapor pressure differences between $C^{12}O$ and $C^{13}O$ and between $C^{12}H_4$ and $C^{13}H_4$ have been measured by Groth, Ihle & Murrenhoff (131) as functions of temperature to gain information on the efficiency of the distillation method for the separation of carbon isotopes. The vapor pressure ratio of $C^{12}O$ to $C^{13}O$ was measured in the temperature range 62° to 74°K. and found to be about 1.01, decreasing with temperature, in good agreement with previous measurements of Kronberger & Johns (132). The vapor pressure ratio of $C^{12}H_4$ to $C^{13}H_4$ is only 1.005 at the triple point. Chloroform, carbon tetrachloride, methyl alcohol, and benzene, have been studied by Baertschi, Kuhn & Kuhn (133) in a more qualitative way, using a distillation column. The more volatile fraction was found to be enriched in the light isotopes Cl^{35} and O^{16}, but the light isotope C^{12} concentrates in the less volatile fraction in all cases. This is not the first time that a light isotope bearing compound has been found to be less volatile than the heavy one; examples have been discussed by Urey (134), who pointed out that a crossing-over temperature may be present in many cases. Many factors are involved in the mass dependence of vapor pressures and no present theory of condensation can account for all the experimental findings. Bradley (135) points out that the crossing-over phenomenon may be due to a competition between a gas-mass-entropy factor and the effect of the zero-point energy of quasioscillation in the liquid. In any case, the field of vapor pressures of isotopic compounds is certainly worth more careful experimental study. Other reports of a less volatile isotopically light species are given by Potter & Ritter (136), for normal and deuterated acetic acid; Morse & Leitch (137), for normal and deuterated 1-chloro-1-propyne; and Nolin (138) for normal and deuterated methyl acetates.

Nolin also gives data on refractive indices, and Dixon & Schiessler (139) report data on density and refractive index for hexadeuterobenzene and (140) viscosity for this compound and for cyclohexane-d_{12}. Zeltmann & Fitzgibbon (141) have measured melting points, boiling points, liquid and vapor densities, and vapor pressures of the deutero-germanes. Giguere (142) has reviewed the properties and structures of H_2O_2 and D_2O_2. Giguere & Secco (143) have studied the system D_2O–D_2O_2 and present a phase diagram of this system and the H_2O–H_2O_2 system. The freezing point curves for the deuterated system are nearly parallel to those for the hydrogen compounds, and are shifted upwards by about 4°C. for water-rich mixtures and 2°C. for peroxide-rich mixtures.

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NUCLEAR AND PARAMAGNETIC RESONANCE[1]

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Advances in electronics made during World War II have resulted in rapid development of the field of radiofrequency spectroscopy. Microwave spectroscopy of gases came first, followed closely by nuclear and electron paramagnetic resonance. One of the major differences between these two types of radiofrequency spectroscopy is that the microwave spectrum measures an intrinsic property of the molecule, its moment of inertia, while the nuclear and electron paramagnetic resonances measure the interactions between the magnetic moments of the nuclei or electrons and the magnetic fields applied to them. If either the field or the magnetic moment is known, the other can be calculated. This flexibility in what is being measured makes the magnetic resonance techniques applicable to a very broad range of problems.

Last year's review by Gutowsky (1) brought the subject of nuclear resonance up to date. Purcell (2) has given a good account of nuclear magnetism for nonspecialists. Recent reviews of paramagnetic resonance have been given by Bleaney (3) and Bleaney & Stevens (4). However, recent activity in these fields has been so great that a full-length joint review is required to report adequately the developments during the past year. The subject matter will be presented in two sections in the order given in the title.

Nuclear Magnetic Resonance

Nuclear magnetic resonance techniques have, from their discovery, been a fruitful means of determining nuclear properties such as the spin and the magnetic moment. The measurement of internuclear distances and angles by studying the magnetic effects of nuclei on one another in solids has been widely exploited. More recently, in liquids, the shifts and complex line structures associated with the electronic environment of the nuclei have begun to be studied, yielding information about the molecular structure, molecular association, and, what is perhaps most important, some information concerning the distribution of electrons in molecules. In these studies, the nucleus serves mainly as a minute probe whose presence does not perturb the system being studied, and from which information can be extracted without appreciably exciting the molecule. Before the applications are discussed in detail, a brief description of the basic phenomenon is perhaps in order.

Theory of nuclear resonance.—When an ensemble of nuclei, each with angular momentum $Ih/2\pi$ and magnetic moment μ, is placed in a magnetic field, H_0, a set of $2I+1$ quantized Zeeman energy levels arises, corresponding to the different orientations of the nuclei. The populations of the levels vary according to a Boltzmann distribution, which, at normal temperatures and

[1] The survey of literature pertaining to this review was completed in January, 1955.

magnetic fields of a few thousand gauss, results in a very slight excess population in the lower levels. Transitions between levels can be induced by application of a small oscillating field, H_1, generated by a radiofrequency coil at right angles to H_0, the static field. The absorption of energy at the resonant frequency is detected as a decrease in the level of oscillation in the regenerative spectrometer of Pound & Knight (5) and Watkins & Pound (6) or as an unbalance in the bridge circuit employed by Purcell *et al.* (7). Since the transitions involve a reorientation of magnetic moments with respect to the magnetic field, the resonance can also be detected as a voltage induced in a second coil at right angles to the first, as in the induction experiment of Bloch (8) and Bloch, Hansen & Packard (9).

The energy of the Zeeman levels is given by the expression $W = -\vec{\mu} \cdot \vec{H} = -\mu H \cos\theta$. The angle θ between the magnetic moment vector and the magnetic field vector is defined by the relation $\cos\theta = m/I$, where m is the magnetic quantum number running from $-I$ to $+I$. Thus,

$$W = \mu H m/I.$$

Transitions are permitted for which $\Delta m = +1$ and therefore $\Delta W = \mu H/I$. The frequency of the transition is found by substituting $h\nu$ for ΔW and obtaining $\nu = \mu H/Ih$. Consequently, a measurement of the field and frequency yields a value for the ratio of the nuclear magnetic moment to the nuclear spin. Observations of the resonance of protons in fields as low as 5 gauss has been reported by Winter *et al.* (10), while use of an ingenious free precession technique permitted Packard & Varian (11) to observe the precession frequency at 2185 cycles in the earth's magnetic field. Accurate frequency measurements permit measurement of the earth's field to a part in 15,000 or better, using the free precession technique.

The solution of some problems in nuclear resonance is facilitated by a transformation from a rotating to a stationary frame of reference, as shown by Rabi, Ramsey & Schwinger (12). A recent case of interest is the effect of perturbing radiofrequency fields on nuclear spin coupling. Bloom (13) transformed to a stationary frame of reference at the P^{31} resonance frequency and calculated the effects of a strong perturbing rf field at that frequency on the F^{19} multiplet splittings and intensities attributable to spin coupling between the magnetic nuclei in the $PO_3F^{=}$ ion. At sufficiently high perturbing rf field strengths the multiplet structure collapsed to a single line. This effect was employed by Shoolery (14) to simplify the complex spectra obtained from boranes as an aid to interpretation, and by Royden (15) as a novel and indirect way of measuring the gyromagnetic ratio of the C^{13} nucleus.

The effect of motion on the width of nuclear resonance lines has been treated by several authors starting with Bloembergen, Purcell & Pound (7). Recently, Anderson (16) has developed a simplified mathematical model of exchange and motional narrowing. Studies of the effect of temperature on the second moments of the proton resonances in *n*-pentane, *n*-hexane, and cyclopentane allowed Rushworth (17) to discuss the most probable types of molecular motions. It is suggested that reorientation of the methyl groups

at the ends of the molecules is important. The activation energies calculated from the data, 2.7 kcal./mole for *n*-pentane, and 2.9 kcal./mole for *n*-hexane, are consistent with this process. Cyclopentane shows interesting behavior in that its second moment decreases below the value calculated for spherically symmetric rotation, and it is thought that the molecules must be diffusing through the lattice. Studies of rubberlike polymers have been undertaken by Honnold, McCaffery & Mrowca (18), who interpreted the variations in line width with curing and carbon black loading in terms of a physical or stearic bond rather than cross-linking.

Relaxation phenomena.—An understanding of nuclear relaxation processes is important because it makes possible the study of the detailed motions in complex systems of molecules through observation of the nuclear magnetic resonances of the nuclei within the system. Gutowsky (1) devoted a section of last year's review to this important subject. Some recent papers on relaxation phenomena merit consideration here.

It is necessary to distinguish between two relaxation times for precessing nuclei. The first, T_1, called the spin lattice or longitudinal relaxation time, depends upon the magnitude of oscillating magnetic fields at the Larmor frequency which exist at the location of the nucleus as a result of the relative motions of the nucleus and other magnetic particles. A change in the longitudinal component of magnetization of the nuclei results in exchange of energy with the thermal degrees of freedom of the system. The coupling mechanism depends upon the properties of the system and the nucleus. In pure solids, lattice vibrations should be the dominant mechanism; in solids with paramagnetic impurities, the large electronic magnetic moment may become the determining factor. Liquids and gases generally obey the theory of Bloembergen, Purcell & Pound (7). Zimmerman (19) has noted an interesting exception for aqueous Mn^{++} ions. However, when the nuclei being studied possess an electric quadrupole moment, the perturbations caused by fluctuations in local electric fields may outweigh all magnetic effects. The symmetry of the molecule containing the nucleus then becomes important. Ayant (20) has discussed the quadrupole broadening of nuclear magnetic resonance lines in liquids, and Van Kranendonk (21) has given a theory of quadrupolar nuclear spin-lattice relaxation in crystalline solids. Finally, in metals, the interaction with unpaired conduction electrons successfully accounts for the measured values of T_1. Bloembergen (22) has extended the theory to semiconductors. Depending upon the statistics obeyed by the carriers, various dependences of T_1 upon temperature are found. Spin diffusion to bound paramagnetic impurities can, in some cases, result in T_1 being independent of temperature. Diffusion of the nuclei in the lattice as a means of spin lattice relaxation has been investigated by Torrey (23, 24).

A second relaxation time, T_2, called the spin phase memory time, or transverse relaxation time, is necessary to describe the changes in the strength of the precessing macroscopic moment vector of the nuclear system as a result of processes which destroy the phase coherence of the microscopic nuclear moments. Local fields from magnetic neighbors and spin exchange between

two nuclei exposed to each other's oscillating field at the Larmor frequency (resulting in a flip-flop process in which energy is conserved) are factors governing T_2 which are internal to the system. The homogeneity of the applied field, H_0, over the sample is an external factor which must be taken into account.

The measurement of T_1 and T_2 has occupied many workers in the field. Free precession techniques, based on a combination of rf pulses, offer the most generally satisfactory method. The averaging procedures used by Hahn (25) in his theory of "spin-echoes" have been modified by Das & Saha (26) yielding, however, substantially the same result. Carr & Purcell (27) have reformulated and extended Hahn's (25) treatment of the effect of molecular diffusion on the measurement. An interesting by-product of their analysis is a method of obtaining a direct measurement of the molecular self-diffusion. Several other authors (28, 29, 30) have proposed new methods of determining nuclear relaxation times. The effect of these relaxation times on the steady state signal shape with a high sweep repetition rate has served as the basis for a method of measuring magnetic field gradients (31).

In liquids of low viscosity, T_1 can become very long, particularly in the absence of oxygen. Giulotto *et al.* (32, 33) measured 3.6 $\pm$0.2 sec. for pure water, and 18 sec. for benzene. A calculation based on the rotation frequency spectrum of benzene yielded 8 sec. The authors suggest that there may be some kind of restrictive potential in benzene which reduces the intensity of the rotational spectrum at the Larmor frequency below that predicted by Debye's theory.

The proton relaxation time, T_1, was studied by Benedek & Purcell (34) for a number of liquids over the pressure range 1 to 10,000 atmospheres. In each liquid, T_1 decreases with increasing pressure, but not simply as $1/\eta$. The observed dependence can be understood if one assumes that the dominant relaxation mechanism involves intramolecular fields, whose correlation time is determined by the rotational freedom of the molecule, and that compression of the liquid restricts migrational motions more severely than rotational motions.

An unusual example of the use of T_1 values to give structural information about a molecule is the measurement by Muller & Bloom (35) of the spin lattice relaxation in liquid menthol (T_1=approx. 0.2 sec.). By choosing a value for the "radius" of the molecule, and modifying the theory of Bloembergen, Purcell & Pound (7) to take account of rotations of CH_3 groups, these authors were able to derive an "average" interproton distance of 1.87 Å.

A mechanism not commonly considered as a factor affecting relaxation times is the radiation damping, or loss of energy to the measuring circuit. Bloembergen & Pound (36) have investigated this case theoretically and have concluded that for the pulse techniques of free nuclear induction, this term can become important, resulting in an early decay of the signal.

The interesting observation was made by Korringa (37) and others (see 36) that the prediction of Overhauser (38) concerning the orientation of

metallic nuclei by saturation of the electron resonance has its counterpart in paramagnetic resonance. Kittel (39) has established a connection between Overhauser's result and the general principles of statistical mechanics. A related experiment has been performed by Honig (40) and treated theoretically by Kaplan (41) in which an As^{75}-doped sample of silicon was irradiated at the electron resonance frequency. Thus, it would seem that whenever the nucleus has its primary relaxation mechanism established through interaction with the electron spin, enhanced orientation of the nuclei will be possible.

Line shapes, widths, and molecular structures.—In single crystals, line shapes are determined primarily by the dipole-dipole interactions between nuclei which lie close together, i.e., the nearest neighbors. A number of components arise whose spacing and intensities determine the shape of the resonance envelope. The broadening attributable to next nearest neighbors, which depends upon their magnetic moments and distances, usually obscures to some extent the details of the line shape. Nevertheless, a complete study of the shape as a function of crystal orientation is capable of locating nuclei relative to one another and to the crystal axes with astonishing accuracy.

In crystalline powder samples, the resonance line shape is determined by averaging the angular dependence over a sphere. The lines are broadened considerably and only internuclear distance information remains. Most recent work, therefore, is of the type in which single crystal information is employed to obtain a rather detailed picture of the crystalline structure.

Considerable difficulty is encountered in obtaining a solution to the equations for systems containing several spins. The calculations are rendered somewhat more manageable when the spins occur in a group with high symmetry. Thus, Bersohn & Gutowsky (42) have calculated the spectrum for a tetrahedral 4-spin system, with I of 1/2, for orientations in which the external magnetic field coincides with a two- or threefold symmetry axis of the tetrahedron, or with a tetrahedral edge. In this way, they were able to demonstrate that in a single crystal of ammonium chloride at $-195°$C., the NH_4^+ ion is oriented with the N—H bonds pointed towards the corners of the unit cube.

Van Vleck (43) has shown that the second moment of the nuclear resonance line can be related to a given structural model. This provides a very powerful method of determining internuclear distances. Gutowsky, Pake & Bersohn (44) computed the N—H distance in NH_4Cl and NH_4Br to be $1.035 \pm .01$ Å from the second moments of the broad, low-temperature proton absorption lines. This can be compared with the more precise results of Bersohn & Gutowsky (42), whose single crystal data yielded the value $1.032 \pm .005$ Å. Variations in the second moment of the NH_4Cl line with temperature permitted studies of the motion of the NH_4^+ ion in the crystal to be made. Hindered rather than free rotational motions were found. Similar studies have been carried out by Deeley, Lewis & Richards (45) with hydrazine salts. A line width transition near 150°K. has been interpreted in terms of reorientation of the $N_2H_6^{++}$ ion about the N—N axis, with a potential barrier of from 3 to 4 kcal./mole. These investigators also studied both

the proton and fluorine resonances of hydrazine fluoride (46) and, from the second moment data, calculated the N—H, and H · · · F distances in the crystal. The N—H distance is 1.075 ± .02 Å compared with 1.03 Å in NH_4Cl, and the difference in the N—H bond lengths is attributed to the very strong N—H · · · F hydrogen bonds. The F · · · H distance of 1.542 ± .01 Å leads to an N—F distance of 2.62 ± .03 Å, in excellent agreement with the x-ray crystallographic value of 2.62 ± .02 Å. Pratt & Richards (47) found that the proton spectra of phosphonium bromide and iodide could be interpreted in value of terms of a P—H distance of 1.42 ± .02 Å. All of these studies illustrate the value of the nuclear magnetic resonance method in locating protons, otherwise very hard to locate accurately because of their low scattering power.

Nuclei with electric quadrupole moments exhibit splitting of the resonance lines as a result of their interaction with crystalline electric field gradients. Since the strength of the interaction depends on the angle of the crystal axes with the magnetic field, it is almost necessary to work with single crystals to avoid smearing the resonance beyond recognition. Even then, the resonance is split into $2I$ components for each value of the field gradient at the nucleus and for each orientation of the molecule in the unit cell. The experimental results are usually compared with theoretical calculations of the number and spacings of the lines in terms of e^2qQ, the strength of the interaction along some chosen axis, and η, a parameter which measures the asymmetry of the field about that axis. The term e^2qQ has the units of frequency, and is generally given in megacycles per second. Recently, studies of sodium chlorate, sodium bromate, and sodium thiosulfate pentahydrate were carried out by Itoh *et al.* (48, 49). The gradient of the field at the sodium nucleus is axially symmetric, and the symmetry axis coincides with that for the halogen nucleus in the chlorate and bromate. The thiosulfate was shown to have different quadrupole interactions at the two sodium nuclei and two groups of molecules with different orientations in the unit cell, resulting in twelve lines. Kernite, $Na_2B_4O_7 \cdot 4H_2O$, was found by Waterman (50) and Blood & Proctor (51) to require four independent sets of quadrupole coupling constants and asymmetry parameters to explain the splittings of the B^{11} resonance. Beryl, $Be_3Al_2Si_6O_{18}$, is being studied by Brown & Williams (52). Cotts & Knight (53) investigated $KNbO_3$ both by this method and by studying the zero field quadrupole resonance of the niobium. Temperatures of phase transitions found in this way agreed well with other known data.

Measurements of the shifts of the resonances from metallic nuclei caused by interaction with the conduction electrons furnish a sensitive indication of changes in the conduction electron wave functions. Although interpretation is sometimes difficult, even qualitative conclusions are of value for testing theories of the metallic state. Knight (54) has observed the shifts of the resonances in Na, Al, Cu, V, and Nb over the range 1.2° to 300°K., concluding that they do not support the assumption of an appreciable electron-lattice interaction. Shifts of the resonances in Cu—Al alloys were also studied by Teeters & Knight (55). They concluded that small solute concentrations act

like impurities and leave the solvent electronic structure essentially unaffected, while undergoing considerable change in their own environment. The line widths in metals were analyzed by Ruderman & Kittel (56), who have developed a theory for line widths resulting from indirect exchange coupling of nuclear moments by conduction electrons.

High resolution nuclear magnetic resonance spectroscopy.—Rapid molecular motions in liquids average the magnetic perturbations of the Zeeman levels to zero, leaving the homogeneity of the applied field as the principal contribution to line width. As the homogeneity over the sample is improved, the resolving power of the nuclear resonance spectrometer increases, and small effects attributable to differences in the electronic environment of the nuclei become measurable. One very important effect is the variation in magnetic shielding observed for chemically or structurally nonequivalent nuclei of the same species, called the "chemical shift." The magnitude of the shift depends upon the strength of the applied magnetic field. In order to avoid the necessity of stating the field strength for each measurement, it has been customary to express the shift as $\delta = (H_r - H_c)/H_r$ where H_r is the magnetic field for resonance in some arbitrary reference compound, and H_c is the field for the compound being studied. The value of δ is then independent of the applied field. Some workers prefer to reverse the sign and write $\delta = (H_c - H_r)/H_r$. The quantity δ then increases with increasing applied sweep field, with increasing electronic diamagnetic shielding, and consequently can sometimes be correlated to some extent with increasing electron density about the nucleus. Both conventions are arbitrary and it would be helpful if one could be agreed upon at a conference on nuclear magnetism.

Ramsey (57) has developed a general theory for magnetic shielding of nuclei in molecules. Both diamagnetic and paramagnetic terms contribute. The paramagnetic term is not readily calculated. Recently, Saika & Slichter (58) proposed a simplified method of applying Ramsey's theory to fluorine chemical shifts. They divided the magnetic field attributable to the electrons into three parts. These were (*a*) the diamagnetic contribution from electrons associated with the atom in question; (*b*) the paramagnetic term resulting from the orbital motions of the valence electrons; (*c*) the contribution from other atoms. For fluorine, (*a*) and (*c*) are much smaller than (*b*). Since *s* electrons exert zero instantaneous orbital magnetic fields at the nucleus, while *p* or *d* electrons exert large ones, term (*b*) is also a measure of the sharing of *p* electrons in the bond formed by the fluorine atom. The degree of sharing a *p* electron is determined by two properties of the bond. These are the hybridization and the ionic character. Data on fluorine chemical shifts and other considerations suggest that the ionic character undergoes more important changes than the hybridization, keeping in mind that these properties serve here only as a description of the state of the electron while close to the fluorine nucleus. On the basis of the above considerations, Saika & Slichter point out that the paramagnetic term would be zero in F^- and reach its largest value in F_2. The theory works very well as a qualitative or semiquantitative correlation of chemical shifts with ionic character in many

fluorine compounds. However, it is necessary to consider a low-lying excited state to explain the shift in UF_6, for which the second-order paramagnetic term is nearly twice as large as that for F_2 (59).

In the case of hydrogen, for which the electron is essentially in an *s* state while close to the proton, terms (*a*) and (*c*) may dominate term (*b*). That this is frequently the case is suggested by the success of various investigators (60 to 63) in correlating the proton shifts with accepted theories of electronic structure. Dailey (64) has recently extended the correlation of nuclear resonance shifts in substituted ethanes with the electronegativities of the substituents (63) with very good success.

Other nuclei studied recently include P^{31}, N^{14}, Cl^{35}, Br^{81}, I^{127}, and B^{11}. Phosphorus alone of these has a spin of 1/2 and zero quadrupole moment. Brother Peter (65) and Gutowsky & McCall (66) have measured phosphorus shifts and analyzed them in terms of the shifts for each atom bonded to the phosphorus, and by considering ionic- and double-bonded electron structures. Broader lines are observed for the nuclei with electric quadrupole relaxation. Sometimes, however, by virtue of molecular symmetry or of similar values of electronegativity for the atoms bonded together, the electric field gradient at the nucleus is small enough to permit high resolution of the order of a few milligauss. In any event, the shifts can usually be measured well enough to permit conclusions of chemical interest. Thus, Masuda & Kanda (67) measured shifts for N^{14}, Cl^{35}, Br^{81}, and I^{127} in concentrated aqueous solutions of HNO_3, $HClO_4$, HCl, HBr, and HI. From these data they were able to deduce something about the degrees of dissociation, and from line width measurements they concluded that undissociated HCl, HBr, and HI molecules are not present as such but exist in some form with much smaller quadrupole couplings.

Rapid exchange of nuclei among different chemical species with different chemical shifts frequently results in a single sharp resonance line located at an average position determined by the time spent in each state. It is fairly easy to show, using the Bloch equations of motion for the magnetic moment vector, that if the average time of exchange is short compared to the reciprocal of the frequency separation of the chemically-shifted resonances, a single sharp line occurs, while if the time is long, two sharp lines spaced by the frequency separation for the two species result. For intermediate exchange times, broad lines occur, as discussed by Gutowsky & Saika (68). Ogg (69) has noted recently that the proton resonance in NH_3 vapor is a triplet; however, the resonance in the liquid is a triplet only under rigorously anhydrous conditions (70). The presence of H_2O is believed to result in rapid chemical exchange of protons between ammonia molecules, distinguishable only by the N^{14} nuclear spin orientation with respect to H_0, and rapid exchange between these results in a single sharp line. With a dilute solution of $NaNH_2$ in liquid NH_3, the systematic broadening of the triplet lines and ultimate narrowing has been followed by increasing concentration, and it was possible to estimate the rate constant for the proton transfer reaction $NH_3+NH_2^- \rightleftharpoons NH_2^-+NH_3$ (70). If more water is added to the system, exchange occurs

between the differently chemically-shifted H_2O and NH_3 species. Thus, the single sharp line from the NH_3 begins to shift with concentration. Gutowsky & Fujiwara (71) have studied this system, and they conclude that deviations from the behavior expected on the basis of simple exchange between free NH_3 and H_2O indicate a dynamic equilibrium involving strongly interacting species.

If rapid chemical exchange is capable of averaging resonance lines, rapid physical exchange of protons in different parts of an inhomogeneous field also ought to be effective as an averaging process. This idea was suggested by Bloch (72) and verified experimentally by Anderson & Arnold (73), who rotated the sample at 25 rev/sec. Only field gradients of appropriate shape and in directions other than along the rotation axis are averaged. Nevertheless, the resolution over the sample of 10^{-4} gauss achievable by this method in a good magnet (of the order of 10^{-2} or 10^{-3} gauss before averaging) has revealed fine structure details hitherto unsuspected, making possible research on a much wider variety of problems.

Multiplet line structures of the type found in ammonia (69) arise because the bonding electrons couple together the spins of the various sets of nonequivalent nuclei. Each resonance is split into $2M_I+1$ components where M_I is the total spin of the nuclei in the other set. The energy of interaction is given by $J_{ij}(\vec{I}_i \cdot \vec{I}_j)$, which results in the spacing of lines being simply J_{ij} cycles/sec. When the chemical shift between the interacting groups becomes comparable to the "spin-spin" coupling, intensities depart from those predicted on the basis of statistical weights of the various spin combinations. This effect has been discussed by Hahn & Maxwell (74) and by Banerjee *et al.* (75), while the effect of molecular electronic structure and molecular symmetry has been treated by McConnell (76). Spin-spin coupling has been observed to traverse four chemical bonds, and in some molecules couples so many nuclei together that several hundred lines occur in the spectrum. In molecules with less extensive coupling the lines appear in characteristic groups which betray the relative positions of the nuclei in the molecule. Analysis of both chemical shift and spin-spin coupling data for unknown systems frequently leads to identification of molecular species, or at least verifies one possibility and rejects others. The method appears to be of considerable value to the organic or fluorocarbon chemist, and to the chemist in search of new physical analytical methods.

Molecular structure models can be quickly verified using nuclear resonance techniques. The boranes have long offered a challenge in this respect. Ogg (77) has discussed the relation of the nuclear magnetic resonance spectra of diborane and borohydride ion to their structures, and has concluded that these data favor the bridge and tetrahedral structures respectively. Shoolery (14) has substantiated the conclusions on boranes by collapsing the spin-spin multiplets with an rf field at the B^{11} frequency. Many molecules containing boron, hydrogen, fluorine, phosphorus, and aluminum appear to be susceptible to this approach.

Other research completed recently includes the work of Alder (78) who

examined the proton resonance in various solutions of electrolytes and found that the shift could be broken down into two parts: a contribution from the polarization of water molecules by the electric field of the ions, and a term attributable to the breaking down of the hydrogen-bonded structure of water. A study of the variation of line width of the proton resonance in $AlCl_3$ solutions with magnetic field strength showed that the water undergoes chemical exchange with a characteristic time of a few milliseconds between solvent and solvated aluminum ions. Jacobson *et al.* (79) examined the line widths and areas of the proton resonance in studying the hydration of deoxyribonucleic acid. The amount of water tied up by the hydration process was inferred from the decrease in area of the proton resonance, an unobservably broad line being assumed for hydrated protons. The addition of electrolytes released water to the normal disordered state with measurable line width, in agreement with observations from dielectric, viscosity, and osmotic pressure studies. Sugawara *et al.* (80) examined the resonance of solid H_2 with various *ortho*-concentrations. They found a coincidence between the temperature at which fine structure appears in the resonance lines and the observed λ-point of the specific heat anomaly in this substance. Hood, Redlich & Reilly (81) measured the shift of the proton resonance in nitric, perchloric, and hydrochloric acids as a function of concentration and deduced the degree of dissociation of these acids. The results were compared with earlier Raman studies, and the assumptions made in making the calculations appear to be justified. Work of this type is beginning to throw some light on the very complex problem of strong electrolytes.

Nuclear spins and magnetic moments.—Nuclear resonance techniques provide a very direct and accurate determination of nuclear spins and magnetic moments. Several new ones have been added recently to the long list of data compiled by early workers in the field. Ag^{107} and Ag^{109} have been measured by Brun *et al.* (82) and by Sogo & Jeffries (83). The former obtained the values $\mu^{107} = -0.113014 \pm 0.000004$ and $\mu^{109} = -0.129924 \pm 0.000004$ nuclear magnetons, while the latter measured -0.113142 ± 0.000013 and -0.129955 ± 0.000013. The determinations were made at slightly different concentrations of $AgNO_3$ and $Mn(NO_3)_2$, and chemical shift and diamagnetic corrections were not made. Brun *et al.* (82, 84) studied K^{41}, Y^{87}, Xe^{129}, and Xe^{131}. The Xe samples were examined under 50 atm. pressure without paramagnetic catalyst. Sogo & Jeffries (85) have also reported values for the magnetic moments of Rh^{103} and W^{183}.

The spin of Si^{29} was reported by Ogg & Ray (86) to be $\frac{1}{2}$, from measurements of the number of peaks in the multiplet arising from the interaction of the proton and Si^{29} spins in SiH_4. A large central peak attributable to the spinless Si^{28} and Si^{30} was flanked by a pair of weak lines corresponding to the 4.7 per cent abundance of Si^{29}. Spins greater than 1 are ruled out directly by this observation, and nuclear shell theory requires a half-integral spin for Si^{29}. Williams, McCall & Gutowsky (87) carried out a similar experiment with enriched SiF_4, reaching essentially the same conclusions.

Instrumentation.—The rotating sample technique developed at Stanford (72, 73) as a means of improving the effective homogeneity of the field represents an outstanding advance in instrumentation for nuclear resonance. Baker (88) has described an rf phase-sensitive detector for use with nuclear induction apparatus which has certain advantages over adjusting the phase of the direct coupling between transmitter and receiver. Richter, Humphrey & Yost (89) describe a method of link coupling the signal generator to the nuclear excitation head. Sherman (90) performed an experiment with a flowing sample of water in which signals were observed with separate regions of excitation and detection. Basically, however, most nuclear resonance apparatus remains in two general categories, the balanced type and the oscillating detector type. The balanced circuits have the advantage of stability of driving frequency and can work effectively at high rf excitation levels. Of these, the crossed-coil nuclear induction circuit maintains a physical rather than an electrical balance and is, therefore, less frequency sensitive. The oscillating detector circuits find application in searching for resonances and in broad line studies where crystal stability is not required.

Other applications.—Applications of indirect interest to chemists include the geophysical exploration which can be conducted with the earth's field magnetometer (11), field control of mass spectrometer magnets for greater stability in high mass work, and measurements of magnetic susceptibilities. Susceptibilities can be determined from the splitting of the resonance from an annular sample (91) or from a sample restricted to two perpendicular planes (92), one parallel and one at right angles to H_0. Speed and accuracy are reported to be very good. Finally, Holder & Klein (93) have described a procedure for obtaining isotope abundance ratios by nuclear magnetic resonance which has yielded very accurate results for paramagnetically relaxed solutions containing the isotopes H^1:H^2 and Li^6:Li^7.

Paramagnetic Resonance

Introduction.—The basic principles of the dynamics of paramagnetic resonance are analogous to those which are used to describe nuclear magnetic resonance outlined above. It should be kept in mind, however, that in addition to the magnetic dipole interactions with the applied magnetic field there may also be exhibited a strong interaction of the spin system, via the orbital angular momentum, with electric fields produced by its diamagnetic neighbors. The quantitative explanations of these interactions by means of wave mechanics and associated experiments have been the result of a very fruitful field of investigation during the past year. Paramagnetism exists in a great many substances: for example, in organic free radicals and in free ions with partially filled electron shells, such as the transition groups; in metals and semiconductors, in plastics, alkali halides, and in glass where unpaired spins result from radiation damage or from the addition of paramagnetic ions.

In the simple case of paramagnetism caused by unpaired electron spins

with angular momentum $\frac{1}{2}\hbar$ and an associated magnetic moment $\mu_\beta = e\hbar/2mc$., the energy of interaction with the applied magnetic field H_0 is given by

$$E = -\vec{\mu}\cdot\vec{H_0} \qquad 1.$$

which is a minimum when $\vec{\mu}$ is parallel to the direction of $\vec{H_0}$. For an electron spin the separations of the energy levels in a field H_0 is given by

$$\Delta E = 2|\mu_Z| \cdot H_0 = g\mu_\beta H_0 \qquad 2.$$

where g is called the spectroscopic splitting factor (4, 94) and is given by the Landé equation, since orbital angular momentum may also be present.

The observation of spin resonance may be accomplished by the introduction into the volume containing the spin ensemble of a radiofrequency field in addition to the polarizing field, H_0. If the frequency of the rf field satisfies Equation 2, then transitions are induced between magnetic levels (e.g., $2S+1$ levels, where S is the total electron spin of the system) with a resultant absorption of energy from the rf field. The influence of this net absorption of energy upon the electronic circuitry coupled to the sample enables the occurrence of resonance to be observed. The relationship between frequency and magnetic field for free electrons ($g=2.0$) is given by the following expression;

$$f\ (\text{mc./sec.}) = 2.80\, H_0(\text{oersteds})\ (94) \qquad 3.$$

For magnetic fields standard in the laboratory the resonances are generally observed at microwave frequencies.

In the case of one of the transition group ions where the paramagnetism results from a partially filled 3D shell, the angular momentum and hence the magnetic moment stems in part from the orbital component and in part from the electron spins themselves.

In any treatment of the quantum mechanical theory of the mechanism of electron spin resonance, the first consideration is the Hamiltonian, and it is important to enumerate and understand the various terms relating to the different interactions of the unpaired spins. For detailed consideration of the theory of paramagnetic resonance the reader is referred to the excellent review of Bleaney & Stevens (4). The types of interaction governing the energy levels of the electrons external to the closed shell of the ion will be only mentioned here and may be classified into the following categories: (4, 95), Zeeman, Stark, exchange, dipole-dipole, spin-orbit, and hyperfine effects. The Hamiltonian may be written then in the following way:

$$\mathcal{H} = \mathcal{H}_{\text{electrostatic}} + \mathcal{H}_{\text{magnetic}}$$

where these may be further differentiated into

$$\mathcal{H}_{\text{electrostatic}} = \mathcal{H}_{\text{stark}} + \mathcal{H}_{\text{exchange}} + \mathcal{H}_{\text{nuclear electrostatic}}$$
$$\mathcal{H}_{\text{magnetic}} + \mathcal{H}_{\text{electon magnetic}} + \mathcal{H}_{\text{nuclear magnetic}} + \mathcal{H}_{\text{rf}}.$$

$$\mathcal{H}_{\text{magn.}} = \mathcal{H}_{\text{Zeeman}} + \mathcal{H}\ \vec{L}\cdot\vec{S} + \mathcal{H}_\beta\vec{\mu}_i\cdot\vec{\mu}_{\beta j} + \mathcal{H}_{\text{nuclear magnetic}}\ (\vec{\mu}\cdot\vec{H}) + \mathcal{H}_{\text{rf}}.$$

It is the combined effects of each of these interactions, which vary in importance according to the physical environment, that are responsible for the

characteristic nature of the observed spin resonance. Such interactions make spin resonance methods useful for the study of many paramagnetic substances, especially those containing ions of the transition elements.

In the case of resonance stemming from the unpaired spins associated with the unfilled shells characteristic of the transition elements, one expects the resonances to be subjected to very strong electrostatic fields. This would be in contrast to the rare earths, unfilled shells of which lie shielded by external electrons.

In the salts of the iron group where the electrons of the 3D shell are exposed, in solids, to the crystalline electric field produced by the neighboring ions, the degeneracies belonging to the $2l+1$ sublevels of a given l of the free ion may be largely lifted. This splitting in the absence of a magnetic field will have important effects on the allowed magnetic transitions observed under conditions of spin resonance upon the application of a magnetic field.

If the nucleus associated with the paramagnetic ion has a nonzero angular momentum and therefore an associated magnetic moment, a hyperfine structure is often observed corresponding to the $2I+1$ (where I is the nuclear spin) magnetic states of the nucleus in the applied strong magnetic field.

In spin resonance spectroscopy the observations of spin resonances are often limited, not by instrumentation, but by the nature of the line itself. The line width of a pure spin resonance is governed by two types of interactions: (*a*) a spin lattice and (*b*) a spin-spin interaction. In the former case there is an exchange of energy with the lattice which is characterized by a thermal relaxation time. The mechanism of energy exchange of the electron spin ensemble with the lattice requires a time-varying magnetic field the Fourier spectrum of which has sufficient energy at the Larmor precessional frequency of the resonating electron to induce transitions between magnetic states. In the case of the electron this "contract" with the environment is often enhanced by the spin-orbit coupling by which the spin feels the thermal vibrations (i.e., variation of electric fields) of the neighboring ions. Theory (96) and experiment show that the thermal relaxation time is strongly temperature dependent. The existence of a strong Stark interaction can also affect the length of the thermal relaxation time by influencing the separation between the ground state and the first excited state of an ion in an electric field associated with a given crystal symmetry.

The second broadening stems from the spin-spin interaction, exchange interaction, or from the effect of neighboring dipoles. This effect is temperature-independent (as long as no phase transitions occur in the crystals) and can be effected through the expedient of magnetically diluting the sample. This spin-spin relaxation time often referred to as the transverse relaxation time (8), arises as a result of the influence of nearest magnetic neighbors generating a field of varying proportions over the spin ensemble such that no single frequency, but rather a distribution, characterizes the resonance condition. This defines an effective line width or the degree of phase coherence of the spin ensemble. Since the above effects govern the intrinsic line width more often than the homogeneity of the magnetic field from the laboratory

magnet, and since resolved lines are desired, high frequencies must be used.

When one wishes to discuss the application of the techniques of spin resonance he finds that the very versatility which makes the method so useful makes it also a rather difficult one on which to write a properly definitive review. An attempt has been made, therefore, to classify the published work of the past year into fields of research with the hope of a minimum of overlap.

Graphite and carbonaceous materials.—Hennig, Smaller & Yasaitis (97) have reported observing resonances in graphite occurring with a g-value of 2.00. A comparison of line intensities with known amounts of hydrazyl indicated a concentration of spin centers of about 10^{-4} per carbon atom at room temperature. The introduction of impurities invariably annihilated the resonance. The authors also found that the line width was affected when the graphite was subjected to electrolytic oxidation in sulphuric acid. The narrowest line recorded was 45 milligauss. It is proposed that the spin centers are probably positive holes trapped at the acceptor state, i.e., the bisulphate radicals. Castle (98), also working with graphite and being careful to align the graphite planes parallel to each other throughout the sample, and placing the sample with the graphite planes parallel to the dc and rf magnetic fields, observed a resonance at a g-value of 2.0056 and with two regions of increased line width near 1700°C. and 2400°C. It is of interest to note that these temperatures roughly correspond to those at which the Hall coefficient for soft carbon solid goes through zero at 1750°C. and 2350°C.

Several authors (99, 100, 101) have studied spin resonance in carbonaceous materials with certain general features becoming apparent. For example, in most such carbonaceous materials, the spin resonance signal was destroyed when the carbon was heated above 600°C. It is suggested (99) that these resonances are not attributable to conduction electrons such as those found in graphite, but rather to unpaired electrons associated with "broken bonds" or free radicals, and that heating above 650°C. enables these bonds to rejoin.

Irradiation of amorphous and crystalline solids.—Livingston *et al.* (102, 103) reported on the measurement of spin resonances attributable to free radicals generated by the irradiation of acids kept at 77°K. One of the radicals formed and trapped in $HClO_4$, H_2SO_4, and H_3PO_4 has been identified as atomic hydrogen. The hyperfine separation agrees extremely well with that obtained from atomic beams. These results indicate that the unpaired electron is well represented by a $1s$ wave function.

Upon closer examination of the hyperfine structure of the proton lines, Livingston & Zeldes observed satellites whose separation from the main line in frequency corresponds to the proton resonance frequency in the field required for the electron resonance at 20 kmc./s. It is proposed that this satellite structure originates from the "flipping" of neighboring proton spins, the flipping rate of which is influenced by the flipping rate of the electrons.

Irradiation of ice (104) at a temperature of the order of liquid nitrogen by Co^{60} γ-rays yields a paramagnetic resonance with hyperfine structure. H_2O ice displays a doublet structure centered about $g = 2.0$ and with a separation of 30 gauss at 350 mc. Using D_2O ice a triplet structure was obtained

with separation of about 15 gauss. These experimental results strongly indicate the presence of an unpaired spin near an H or D nucleus. Since the splittings are considerably less than the free atom values (see Livingston above) it is suggested that the unpaired spin is actually a free electron trapped in the neighborhood of the H or D nucleus. Further measurements at 4°K. indicate additional hyperfine structures which may be attributed to the presence of OH radicals in the crystalline solid.

The investigations of the effects of radiations on alkali halide crystals have for some time received considerable attention with an aim to correlating the results from optical absorption bands with the evidence obtained from the resonance of the unpaired spins established at radio frequencies. Jen & Lord (105) and Schneider (106) have reported on their investigations with irradiated LiF crystals. Spectrophotometric methods show the normal *F*-band at 2480 Å with color center concentration varying from 5 to 13×10^{16}/cc. (106). The electronic resonance has a complex structure with a *g*-factor slightly larger than the free electron for an intense central peak. In addition to and superimposed on the single line was a much weaker pattern of 19 narrower lines usually spaced at about 60 gauss intervals. Schneider proposes that the broad peak is associated with the *V*-centers and the 19 line patterns with the *F*-centers. The pattern is interpreted as resolved hfs due to the interaction with the neighboring Li nuclei.

The production of lattice defects in diamond and smoky quartz has been reported on by Griffiths, Owen & Ward (107). Their measurements in neutron-irradiated diamond revealed an isotropic line at approximately the free electron value, which line was somewhat temperature sensitive, being materially reduced upon heating the diamond to 1000°C. An anisotropic spectrum, consisting of lines symmetrically arranged about the above isotropic line, was observed not to be affected by heating and is thought to be a result of a system of spin, $S=1$, with the levels being split by an electrostatic interaction of the crystalline field of axial symmetry.

The rather complex nature of resonances observed in smoky quartz indicate that there are at least six types of paramagnetic units all of which are removed by heating the quartz to 350°C. Each of the six absorption lines appears to be subdivided into six lines of roughly equal intensity. It is possible that this is hfs and that the magnetic centers are electrons moving in orbits associated with atoms of nuclear spin 5/2.

Uebersfeld (108, 109) has remarked on the effects of bond damage in certain organic molecules. Particularly in the case of amino acids, he has observed a resonance consisting of three lines, intensities of which suggest an interaction with a nuclear system of spin one. Uebersfeld proposes that the free radical is created in the neighborhood of a CH_2 bond and that the hfs results from interaction with the neighboring two protons. Evidence that the hfs does not stem from the N^{14} nucleus was suggested from the fact that the pattern was unaltered when the N^{14} nucleus was substituted by 33 per cent N^{15} ($I=\frac{1}{2}$).

Resonance lines were observed also in irradiated plexiglass (108) and

glass (110). Heating of the glass samples to 150°C. caused the lines to disappear. For further comments on paramagnetic resonance in glass, see below under the section on transition elements.

Metals and semiconductors.—The extreme sensitivity characteristic of the method of spin resonance at microwave frequencies in the 10 and 20 kmc. range permits the detection of very low concentrations of spin centers. In particular, this sensitivity brings the method within the range of donor concentration (40, 41, 111, 112, 113) of semiconductors. Fletcher *et al.* (111, 112) at Bell Telephone Laboratories and Honig (40) and Kaplan (41) at the University of California have reported some very interesting effects associated with the interactions of conduction electrons of the semiconductor and nuclei employed as "doping" agents in the "host" conductor. Experimental evidence that the hfs is actually associated with the impurity nucleus was supplied from the fact that when P^{31} ($I=\frac{1}{2}$) (111, 114) was added to the host instead of arsenic the resonance had just two peaks. Similarly, doping with antimony revealed an hfs associated with the two antimony isotopes. A detailed examination of the spectrum of antimony by Fletcher *et al.* in silicon metal revealed the presence of weak satellite lines which the authors attribute to forbidden transitions (cf. 103).

Honig (40) has observed the hfs of resonance in arsenic-doped metal (concentration of 1.3×10^{17}/cc.) at 4°K. and at a frequency of 9 kmc./*s.* and reports that these lines exhibit an inhomogeneous saturation behavior. The proposed explanation by Kaplan (41) of the enhancement of the second line of the hfs relative to the first utilizes the process whereby the electron spin relaxation can affect a nuclear spin reorientation through $\vec{I}\cdot\vec{S}$ magnetic interaction.

At the time of this writing experiments are under way (specifically, by Kip at University of California, Fletcher at Bell Telephone Laboratories) in an attempt to repeat the measurements of Honig. Other theoretical considerations suggest that the mechanism proposed by Kaplan to explain Honig's experiment is probably not responsible for the effect observed and that the expected polarization is much less than 100 per cent.

Elliott (115) has published his theoretical calculations designed to explain the variation of *g*-values and line width of spin resonance resulting from impurities in semiconductors with the material and impurity concentrations. A theory has been developed which takes into account the effect of spin-orbit coupling.

Gutowsky & Frank (116) have measured absorption line shapes in Li and Na particles suspended in mineral oil at 25 mc. and report a Lorenztian line shape but with a distortion on the low field side attributed in part to the use of a ω_0 less than the total half width.

Quantitative measurements of the susceptibility caused by spin polarization are in general rather difficult to perform partly because of the unknown instrumental parameters. Schumacher *et al.* (117) have performed this measurement in a rather novel way. They have measured the total area under the absorption curve for the electronic resonance and then compared this area

with that obtained from the nuclear resonance curve, keeping the frequency (17 mc.) constant and all instrumental parameters the same, excepting H_0, which runs from a few gauss for the electrons to 10 kilogauss for Li^7 nucleus. From knowledge of the nuclear susceptibility, the ratio of absorption areas and the gyromagnetic ratio of the electron and nucleus an experimental value for $\chi_{spin} = 2.0 \pm 0.3 \times 10^{-6}$ cgs. vol. units was obtained. A theoretical calculation (118) for electron spin-only susceptibility yielded a value of 1.87×10^{-6} cgs. units with 20 per cent error.

Feher & Kip (119) and Feher & Griswold (120) have reported on spin resonance of Be, Li and Na where their measurements on T_2 take into account the finite particle size of the sample relative to the skin depth of the rf field.

Transition elements.—The paramagnetism associated with those substances containing members from the iron group originates from the unfilled 3D shell of the atomic ions. Because these unpaired 3D spins are not shielded by external valence electrons, the character of the observed resonance spectra is quite sensitive to the environment of the ion and often reveals considerable information as regards the electric field symmetries. The comparison of experimentally observed spectra with wave mechanical descriptions of the paramagnetic salt often permits the evaluation of the relative importance of the various interaction terms in the spin Hamiltonian (cf. 4, 95). Several authors (121 to 126) have used salts containing paramagnetic ions to advantage for the study of the symmetry of the crystalline fields and crystal lattice constants from the relative magnitude of the interactions. The study of the paramagnetic resonances of manganous ion and the disappearance of the hfs in the formation of complexes has been used by Cohn & Townsend (127) as a means of gaining an insight into the type of bond involved with complexes of this ion. It was found that the signal amplitude was a linear function of the concentration of the Mn^{++} ion in the range of 0.001 to 0.01 *M*. The existence of an hfs for the Mn^{++} is generally explained by the "promotion" of one of the normal 3*S* electrons to the 4*S* orbital. If the 4*S* orbital of Mn^{++} is occupied by an electron donated by other atoms in the complex, as it would be for any type of covalent bond formation, there would be no admixture of 4*S* and hence no hfs. Changes in static susceptibility are limited to those compounds in which the 3D electrons are changed.

The presence of Mn^{++} in phosphors has been observed and reported on by Uebersfeld (128). The characteristic hfs attributable to the Mn nucleus ($I = 5/2$) was observed. Hurd *et al.* (129) working with $CaCO_3$ crystals containing 0.06 weight per cent of Mn^{++} recorded a spectrum consisting of 30 well-resolved lines approximately 3.5 gauss in width and extending over a range of 1100 gauss. The spectrum has a large dependence upon angular orientation between crystal axes and external magnetic field. The interpretation of the observed spectra is based upon the crystalline field effects plus nuclear hfs.

Bleaney & Trenam (130) have studied the spin resonance in ferric rubid-

ium sulphate and ferric potassium selenate alums. They were unable to detect any evidence of hyperfine interactions with Fe^{57} in a sample containing 40 per cent enrichment of this isotope. From an analysis of the line shape an upper limit could be placed upon the overall widths of any such structure which would correspond to a nuclear moment of 0.05 n.m.

Sands *et al.* (95, 131) at Washington University have reported the presence of spin resonances in many types of glass. The various samples of glass with known amounts of impurities show absorption lines with apparent g-values of 2, 4, and 6. The general shape of the resonances can be explained by postulating a spin Hamiltonian containing terms involving Stark interactions In some instances hyperfine interactions with the nucleus of the paramagnetic impurity were also evident.

As a further example of the applications of the paramagnetic resonance technique to the study of the solid state, Hornig *et al.* (132) reported the observations of a resonance spectrum containing many components in single crystals of the ferroelectric $BaTiO_3$. The presence of the spectra is attributed to small amounts of iron added to the premelt mixture. The resonance frequency and amplitudes of the predominant lines are reported by the authors to be sensitive to temperature and in particular indicative of the crystallographic state of the $BaTiO_3$. The resonant lines are quite anisotropic and sensitive to the orientation of the axis of polarization relative to the external magnetic field. The explanation proposed for the spectrum is one of strong Stark splitting of the $^5D_4$ basic level of the ferrous ion.

Organic free radicals.—As indicated in the introduction in this section, another source of unpaired spins is that of organic free radicals, which may be sufficiently stable at room temperature to permit observation with resonant equipment. The technique of spin resonance is particularly useful in the field because it permits an independent nondestructive detection and analysis of the free radicals during the time when, for example, certain changes are being induced in the chemical environment of the sample (133).

A new class of compounds exhibiting paramagnetic resonance called biradical-molecular compounds has been studied by Kainer, Bijl & Rose-Innes (134). A mechanism is proposed whereby a strong oxidizing agent and a strong reducing agent normally diamagnetic are bonded together with chiefly ionic forces and a resonance between a diamagnetic and paramagnetic form is necessary for stability. The paramagnetic level must be sufficiently low to be populated at room temperature. Their resonant measurements (at 90°K.) on several molecular complexes, of which *p*-phenylenediamine with tetraiodo *p*-benzoquinone is an example, indicate the existence of unpaired spins.

A rather detailed study of spin relaxation in free radical solutions has been made by Lloyd & Pake (135). Experimental studies of the spin-lattice relaxations in aqueous solutions of the free radical peroxylamine disulfonate ion $ON(SO_3)_2^{--}$ were made at a field near 30 gauss (60 mc./sec.). The definition of a unique relaxation time was complicated because of the hfs, resulting from interactions with the N^{14} nucleus. General treatment of the saturation

method [cf. Bloch (8)] leads to a definition of the relaxation probability. The theory rules out the interaction of the electrons with other protons of the H_2O solvents as well as the quadrupole interaction of the N_{14} nucleus. Estimates have been made of the role of the spin-orbit coupling, and it appears probable that the observed relaxations involve this interaction.

The observed hfs of spin resonance of carbazyl and hydrazyl in solution by Kikuchi & Cohen (136; see 137) show that in carbazyl the two N-atoms are nonequivalent in that the unpaired spin spends approximately twice as long in the vicinity of one as compared to the other. The spin resonances in Wursters Blue and Red are perhaps the most complex of the resolvable structures. For, according to Weissman (138), he has observed as many as 39 lines composed of three sets of 13. An unambiguous assignment of the origin of most of the splittings could not at the time of publication be made. Certain metal organic compounds (139) also yield resonances characteristic of the transition elements involved.

Measurements (140) on diphenyl-trinitrophenyl hydrazyl at temperatures down to 1.6 °K. yield a g-value of 2.00. Paramagnetic absorption in free radicals has been observed down to very low magnetic fields (141) (frequency corresponding to as low as one mc./sec.) For each radical the entire shape is accurately predicted by a set of modified Bloch equations.

Basic to the method of spin resonance is the unequivocal measurement of the paramagnetic properties of a material as compared to the nonresonant methods of measuring the total macroscopic susceptibility. In this way small amounts of paramagnetism may be detected in materials whose susceptibility is determined by other means to be diamagnetic. Yokozawa & Tatsuzaki (142) have recently reported detecting resonances in polynuclear aromatic hydrocarbons, violanthrone and violanthrene. The smaller value of the diamagnetic susceptibility of the former, when compared with the latter, may be accounted for by the observed intensities of the spin resonance lines in these compounds. The intensity of the resonance in violanthrene is too small to be significant in the total magnetic susceptibility.

Free radicals have been observed in biological materials by Commoner, Townsend & Pake (143). The results show that these free radicals occur in plant and animal tissues and provide evidence relating them to metabolic activity. As an example, it was reported that etiolated barley leaves show only about one-fifth the resonance absorption observed in fully green leaves. The number of unpaired spins observed in these materials ranged from 10^{-8} to 10^{-6} moles/gm.

Other chemical compounds.—One of the important uses of spin resonance is in the measurement of nuclear spins and magnetic moments via the hyperfine interaction in compounds where the paramagnetism of the ion precludes the use of nuclear magnetic resonance. The Oxford group (144 to 147, cf. 148) have exploited this interaction for the determination of nuclear spin, by merely counting the number of lines, for the measurement of the ratios of nuclear magnetic moments of isotopes, and for the estimates on the actual values of the magnetic moments. Measurements on single crystals of

$PuO_2Pb(NO_3)_3$ (144, 148) at 3.2 and 1.5 cm. and at 20°K. yield a spin of $\frac{1}{2}$ for Pu^{239} and a provisional value for $\mu(Pu^{239})$ of 0.5 ± 0.2 n.m. The hyperfine structure (145) of the Nd^{3+} ion, attributable to the two odd isotopes 143 and 145, has been measured with the result $\mu(143)/\mu(145) = 1.6083 \pm 0.0012$. Approximate theory yields a value of 1.0 ± 0.62 n.m. for the moments of the isotopes 143 and 145. Measurements (146) at 10° to 20°K. on single crystals of $(UO_2)Rb(NO_3)$, containing 40 μg. of the plutonium isotope 241, yield six equally-spaced lines with a field separation of 245 ± 1 gauss, indicating $I\,(241) = 5/2$. The separation of the two hyperfine lines arising from the isotope 239 (observed in the same crystal) was of the order of 347 gauss. Estimates of the magnetic moments from an analysis of the Hamiltonian yield $\mu(239) = 0.4 \pm 0.2$ n.m. and $\mu(241) = 1.4 \pm 0.6$ n.m. The ratio of magnetic moments of the two isotopes was observed to be 3.53 ± 0.02. For the spin of Np^{237} Bleaney (147) reports $I\,(Np^{237}) = 5/2$ with estimated $\mu(237) = 6 \pm 2.5$ n.m.

Ghosh, Gordy & Hill (149) report observing extremely broad absorption lines in uranium salts with apparent width of the order of several kilogauss. Gijsman *et al.* (150) have used the paramagnetic resonance technique to investigate the magnetic properties of bivalent silver in persulphates stabilized in pyridine. A resonance was observed of $g = 2.08$ with a width of 70 gauss. Spin resonance (151) in single crystals of gadolinium sulphate reveal two independent spectra, indicating that there are two magnetically nonequivalent ions per unit cell.

Special effects.—In this category are discussed those effects associated with spin resonance wherein the emphasis of the investigation did not warrent consideration in the preceding sections. Several authors (cf. footnote of 39, 115, 135, 152) have published papers covering theoretical considerations governing the relaxation times of paramagnetic resonance. Bloembergen & Wang (153) discussed their experiments and theoretical considerations of the relaxation effects in para- and ferromagnetic resonance, with particular attention to the transfer of energy and spin-exchange systems (above the Curie point), when large exchange interaction occurs between spins.

Paquett (154) has measured the influence of the establishment of resonance on the rotation of the plane of polarization of visible light (Faraday effect) as it passes through a paramagnetic salt. Kastler (155) has measured the sign of the electronic gyromagnetic ratio by observing resonance in a purely rotating magnetic rf field.

Beringer & Heald (156) have measured accurately the ratio of the electronic to the proton g-factors by a precision microwave absorption technique. The result obtained was $-g_s/g_p = 658.2277 \pm 0.0002$, where g_p refers to protons of molecular hydrogen and g_s refers to the electron of atomic hydrogen. The microwave frequency was determined by multiplying up from a standard 100 kc. source and beating with the microwave generator. The magnetic field was measured and controlled during the experiment by a proton signal.

Garstens (157) and Garstens *et al.* (158) have made a classical analysis of paramagnetic resonance in gas at low fields. It is assumed that the gas is

composed of an ensemble of magnetic dipoles in an external magnetic field, with either a circularly or linearly polarized rf field at right angles to the polarizing field. Taking into account the effect of collisions, the absorption formulae thus derived predict a change in the apparent g-value from the free spin value, varying inversely with $\omega\tau$ (τ is the collision time) from the fourth power when $\omega\tau > 1$, decreasing as $\omega\tau$ approaches 1, and then increasing as $\omega\tau < 1$.

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STATISTICAL MECHANICS[1]

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Introduction

The methods of statistical mechanics are at present so widely used that any exhaustive review article on statistical mechanics would cover a great deal of the whole range of theoretical physics and physical chemistry. For this reason, the title of this review article would be better "Selected Topics in Statistical Mechanics." In this selection, we have tried to concentrate on the subjects to which interesting contributions have been made in the last year. We have tried to devote more space to the papers which introduce new ideas than to papers which develop ideas contained in earlier papers. But, of course, this distinction is often difficult or impossible. Finally, in spite of our effort and the help of our co-workers, there may be many papers we have overlooked. We wish to apologize for this.

I wish to express my appreciation to Dr. R. Brout, Mr. R. Bingen, and Mr. J. Jeener for their active help in this work. The whole of Section 3 on Statistical Mechanics of Irreversible Processes has been written in cooperation with Dr. Brout. Mr. Bingen has reviewed the papers on the Vibration Spectrum of Perturbed Lattices (Section 4, par. d), and Mr. Jeener has helped in the preparation of Section 5 on Liquid Helium. In addition, I express my gratitude to all my co-workers in my department who have taken over the whole task of literature search.

Before going into the description of the literature on a specific subject, we wish to mention the books on statistical mechanics which appeared in 1954. The first is that of ter Haar (1). The main feature of his "Elements of Statistical Mechanics" is the large number of interesting applications which are treated in detail. They include such widely different subjects as semiconductors and statistical methods in nuclear physics. The "Molecular Theory of Gases and Liquids" by Hirschfelder, Curtiss & Bird (2) is a basic contribution to the literature of statistical mechanics. Any short analysis would do injustice to it. It is the best reference treatise for any question pertaining to equations of state, intermolecular forces, or transport properties.

Phenomenological Methods—Thermodynamics of Irreversible Processes

We shall review in this section some papers situated on the border line between macroscopic thermodynamics and statistical mechanics.

It is well known that the principle of microscopic reversibility plays a vital role in the derivation of the famous Onsager reciprocity relations

[1] The survey of the literature pertaining to this review was concluded in January, 1955.

(3, 4, 5). In an interesting paper Thomsen (6) has studied in detail a simple statistical model for which the equations of change are given by the first order differential equations

$$\dot{P}_i = \sum_j (P_j\lambda_{ij} - P_i\lambda_{ji}) \qquad 1.$$

(P_i probability that a system chosen at random will be in state i, λ_{ij} conditional transition probability per unit time of a system going from state i to state j).

Thomsen defines the following five propositions:

(*a*) Microscopic reversibility (M)

$$\lambda_{ij} = \lambda_{ji}; \qquad 2.$$

(*b*) Detailed Balance (D) requiring that transitions between two states take place with equal frequencies at equilibrium

$$P_i\lambda_{ij} = P_j\lambda_{ji} \text{ (at equilibrium)}; \qquad 3.$$

(*c*) The Ergodic Hypothesis (E) which assumes that all states are equally probable at equilibrium;

(*d*) The Second Law of Thermodynamics (S) which states that the entropy of an isolated system never decreases;

(*e*) The so-called λ hypothesis (L) which assumes that the sum of all elements in a given row of the transition matrix is equal to the sum of the elements in the corresponding column

$$\sum_j \lambda_{ij} = \sum_i \lambda_{ji}. \qquad 4.$$

The various logical relationships between the above propositions are then considered. It is easily shown that (E), (L), and (S) are equivalent, and that (M) is equivalent to (D) and (E) together. This shows very clearly that the requirement of (E) or (S) alone does not rule out the possibility of circular processes like

characterized by the transition matrix

$$\lambda = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}.$$

This transition matrix satisfies (L). Also one sees very directly why microscopic reversibility is a stronger condition than the Second Law.

As Casimir (4) has pointed out, Onsager's original proof is only strictly valid for scalar irreversible processes (like chemical reactions or relaxation phenomena) for which the irreversible fluxes may be considered as time derivatives of thermodynamic state variables. This is not correct for vectorial

phenomena (like heat conductivity) or tensorial processes (like viscous flow). Casimir (4) has proposed a method to avoid these formal difficulties and has shown that the correct form of Onsager's reciprocity relations is for heat conductivity in anisotropic media, (in absence of a magnetic field)

$$\sum_{\mu} \frac{\partial \mathrm{L}_{\mu\nu}}{\partial x_{\mu}} = \sum_{\mu} \frac{\partial \mathrm{L}_{\nu\mu}}{\partial x_{\mu}} \qquad 5.$$

where L is the heat conductivity tensor. The physical content of 5 is that the antisymmetric part of L has a vanishing divergence and so does not give rise to experimentally observable effects.

Casimir's method introduces equations for the regression of an infinite number of local temperature fluctuations. Then Onsager's method can be used because the rates of the irreversible processes are the time derivatives of the state variables (the local temperatures), but the relations found in this way are not directly applicable because the equations for the regression of the local temperature are not identical to the macroscopical Fourier equation

$$c\Delta\dot{T}(\mathrm{r}) = \mathrm{div}\,\{\mathrm{L}(\mathrm{r})\ \mathrm{grad}\ \Delta T\} \qquad 6.$$

and the corresponding Onsager relation has still to be transformed into 5.

This method has also been applied by Mazur & de Groot to electrical and heat conduction in the presence of a magnetic field (7). However, more recently de Groot and Mazur (8) have developed an alternative method which avoids the intermediate step (eq. 6) of Casimir's treatment. The fluctuation formalism used by Onsager is combined directly with the basic macroscopic equations (9, 10) (conservation of mass, momentum, and energy and entropy production in local form). The reciprocity relations of the form 5 are obtained in a straightforward way. The new derivations of Onsager's relations have been published by Wigner (166).

One of the most interesting applications of thermodynamics of irreversible processes is the "Theorem of minimum entropy production" (9, 10, 11). This theorem states that the steady state of an irreversible process is characterized by a minimum value of the rate of entropy production compatible with the external given constraints. These external constraints (e.g., an externally maintained temperature difference between different parts of the system) prevent the system from going to equilibrium. Let us call

$$\mathcal{P} = \frac{d_i S}{dt} \qquad 7.$$

the entropy production per unit time. The most important properties of $\mathcal{P}$ are

$$\mathcal{P} \geqq 0 \qquad 8.$$

$$\mathcal{P} = \text{minimum in stationary state} \qquad 9.$$

$$\frac{d\mathcal{P}}{dt} \leqq 0 \qquad 10.$$

Property 8 remains true under the most general conditions, being an expression of the second law of thermodynamics. Properties 9 and 10 are

the formulation of the theorem of minimum entropy production. The demonstration of this theorem involves the following assumptions:

(*a*) Linear phenomenological relations between generalized forces [chemical affinity in the sense of De Donder (12, 13, 14) gradients of temperature, e.g.,] and rates of irreversible processes;
(*b*) Onsager's reciprocity conditions;
(*c*) phenomenological coefficients being constant. For continuous media (15, 16, 17) it is also necessary to suppose mechanical equilibrium.

Klein & Meijer (18) have recently treated in detail a simple example of a steady-state, the thermomolecular pressure, i.e., the flow of matter and energy through a narrow tube connecting two containers maintained at slightly different temperatures. This problem can be readily studied by a statistical method similar to that used by Thomsen (6) (cf. eq. 1) starting with a set of equations which give the time variation of numbers of molecules in the energy states of the two containers. Klein & Meijer prove that, in accordance with the theorem of minimum entropy production, the steady-state corresponds to that set of occupation numbers which minimizes the rate of entropy production.

For chemical reactions the conditions enumerated above are only satisfied "near equilibrium," i.e., where the stationary state is near an equilibrium state.[2]

For open systems far from equilibrium, the entropy production is, in general, no longer minimum in the steady-state. Examples of this behavior have been discussed by Denbigh (20) and Nielsen (21). However, Mel (22) has shown that the properties of the entropy production are not completely lost. For large classes of chemical reactions $\mathcal{P}$ always decreases if the system is far from the stationary state whatever the position of this stationary state with respect to true equilibrium. Let us consider the change of $\mathcal{P}$ with time. This change may be written as the sum of two parts. The first, $d_X\mathcal{P}$, is related to the changes of the generalized forces with time and the second, $d_J\mathcal{P}$, to the change of the rates of the irreversible processes. It is then possible to derive the following two theorems [Glansdorff & Prigogine (23)]; (*a*) If the restrictive conditions necessary for the validity of the theorem of minimum entropy production are satisfied, both parts are equal and decrease in time. (*b*) If only mechanical equilibrium and time independent boundary conditions are postulated, the first part (related to the change of the generalized forces) is always negative or zero. The change of generalized forces is therefore such that it lowers the value of the entropy production. This behavior is closely related to the classical stability conditions of equilibrium (14).

Another approach to the problem of variational principles for irreversible processes consists in the study of functions which satisfy the conditions

[2] If we consider a sequence of chemical reactions it is sufficient that the affinity of each individual step is sufficiently small (19).

8 to 10, i.e., a wider domain in which some of the restrictive conditions stated above are no longer satisfied (24). For instance, one can show quite easily that stationary states in the problem of thermal conductivity with prescribed time independent temperatures at the boundaries are characterized by a minimum of the integral [Prigogine (24)]

$$L = \int_V \lambda^2 (\text{grad } T)^2 dV = \int_V W^2 dV \qquad 11.$$

where λ is the coefficient of thermal conductivity and W the heat flow. This function L satisfies all conditions 8 to 10. In the neighborhood of equilibrium L becomes proportional to the entropy production per unit time. The variational principle 11 has a very simple physical meaning: in the stationary states the average value of the square of the thermal flow is as small as possible. Unfortunately, the precise choice of the Lagrange function L far from equilibrium seems to depend in general on the mechanism of the irreversible processes. We see, however, (22, 23, 24) that even outside the validity of the theorem of minimum entropy production, thermodynamic functions play a determinant role in the direction of evolution toward the stationary state.

The detailed description or enumeration of recent applications of thermodynamics to irreversible processes is outside the scope of this review paper. We may just mention the investigations by Meixner (25) on the thermodynamical theory of relaxation and its relations to more general theories of aftereffects based on the superposition principle by Boltzmann.

The macroscopic theory of thermoelectric, thermomagnetic, and galvanomagnetic effects has been considered by various authors (26 to 29), continuing previous work by Callen (30), Mazur & Prigogine (31) [cf. also (10)]. The thermodynamics of irreversible processes in thermocouples and thermocells (32) and in rotating systems (33, 34) has been developed.

The possible extension of the local formalism of thermodynamics of irreversible processes to irreversible processes associated with internal degrees of freedom has been considered (35). Interesting applications of concepts of thermodynamics of irreversible processes to surface tension of mixtures out of equilibrium [Defay (36)] and to thermal diffusion in liquids [Alexander (37)] have been published. Considerations of irreversible processes in systems in an electromagnetic field have clarified the controversial question of the driving "force" in electrochemistry (38 to 42). Only for an observer who moves with the center of mass and at stationary state does it reduce to the gradient of the electrochemical potential used by Guggenheim (43) and others. An interesting study of thermodynamic effects associated with a magnetic field has been published by Hanszen (44).

Statistical Mechanics of Irreversible Processes

Van Hove (45) has written an important article in which he relates neutron scattering cross-sections to space-time correlations in many-particle

systems. Neutrons, unlike photons or electrons, possess mass comparable with nuclear masses and hence may readily exchange energy with the scattering system. Thus, inelastic collisions are of frequent occurrence in neutron scattering. Therefore, one may measure, in addition to the angular distribution of scattered particles, their energy spectrum. Van Hove has shown that, in Born approximation, the 4-dimensional space-time Fourier transformation of the scattering cross-section is a certain distribution function $G(\mathbf{r}, t)$ characteristic of the scattering system. This function is readily interpreted in the classical limit as the average density distribution at time t as seen from a point which was occupied by a particle at time 0. In the limit as $t \to 0$, $G(\mathbf{r}, t) \to \delta(\mathbf{r}) + g(\mathbf{r})$ where $\delta(\mathbf{r})$, the Dirac δ function expresses the certainty of a particle being at $\mathbf{r} = 0$ when $t = 0$ and $g(\mathbf{r})$ is the familiar time-independent distribution function. For homogeneous systems $\lim_{t\to\infty} G(\mathbf{r}, t) = \rho$ where ρ is the density of the system. For intermediate times, it is demonstrated that the time variation of G affects the scattering distribution only for a particle spending at least a time of the order of the characteristic relaxation time of the system over the characteristic correlation length.

An interesting semiquantitative macroscopic calculation of $G(\mathbf{r}, t)$ is made for the critical region of liquids. The phenomenological laws of viscosity and heat conduction are used in conjunction with the time-independent critical fluctuation theory of Ornstein & Zernike (46). This allows one to make some qualitative predictions about neutron scattering in the critical region, viz., very abundant scattering and anomalous wavelength dependence.

The paper also contains an analysis of neutron scattering in crystals and in quantum ideal gases. The asymptotic behavior of $G(\mathbf{r}, t)$ for large times in crystals is studied. Van Hove shows that it reaches its equilibrium value according a $|t|^{-3/2}$ law. This implies that the crystal, despite its overall lack of ergodicity, exhibits a kind of local return to equilibrium ("local ergodicity"). Such kind of behavior has been studied in a paper by Klein & Prigogine (47) to be reviewed below.

In a subsequent paper, Van Hove (48) discusses neutron scattering in ferromagnets. Here the magnetic moment of the neutron interacts with the electron spin system of the crystal. It is shown that $G(\mathbf{r}, t)$ is a superposition of two parts; one is the correlation function of the nuclei, examined in the previous paper, and the other is the time-dependent correlation between spins. The qualitative behavior of the scattering is predicted from deducible properties of the spin correlations, and agreement with experiment is found. Of considerable interest is the discussion of scattering near the Curie point. As in liquid critical scattering, Van Hove has used a macroscopic formulation. The time-independent formalism is that of the macroscopic cell fluctuation theory of Klein & Tisza (49). For the time dependence, one again assumes a phenomenological decay law. It is then deduced that neutron scattering due to critical fluctuations should be experimentally detected above the Curie point for scattering angles slightly rotated from the Bragg

angle (the latter to remove the large coherent scattering from the lattice). This prediction has been verified experimentally.

Klein and Prigogine (47) have continued their work on the statistical mechanics of irreversible processes (50). A detailed study has been made of linear assemblies of harmonic oscillators with nearest neighbor interactions. The equations of motion have a particularly simple solution, which allows one to trace probability distribution functions in time. In spite of Liouville's theorem and reversible behavior of the system as a whole, local distribution functions (that is, pertaining to a finite group of velocities and positions) show a remarkably simple asymptotic behavior. For all cases in which initially there does not exist correlation over ranges comparable to the total length of the system, these distribution functions tend to multivariant Gaussian distributions. All the higher cumulants decay to zero. The second moments do not have, in general, the values corresponding to thermal equilibrium except in the special case in which initial equipartition of the energy of the normal modes (in classical mechanics) has been assumed.

This behavior shows, as in Van Hove's work (45), the existence of a kind of local ergodicity. This opens the possibility of defining entropy and H theorem in terms of local distribution functions without an appeal to other assumptions (i.e., coarse grained or time smoothed distribution functions).

It is also shown that the correct mechanical behavior is at variance with that predicted from the formalism of Born and Green, using the superposition approximation. The reason is that in the course of time successive correlations develop which are zero in the Born-Green formalism (51). These correlations asymptotically go to zero, but it is the neglect of them for intermediate times that makes the Born-Green result incorrect. It is not insignificant that, for short times, the Born-Green equation gives correct results. Physically, there has not been sufficient time in this approximation to establish more distant correlations than between two neighbors.

The problem of deducing, from quantum mechanical laws the usual first-order differential equations which describe the approach to equilibrium is studied in an interesting paper by Van Kampen (52).

The current derivation is due to Pauli (53, 54). The Hamiltonian of the total system is split up into a nonperturbed part $H^{(0)}$ and a perturbation V for the interaction. Dirac's theory of time-proportional transition is then applied. For this reason the usual method is only applicable for short times (in comparison with the time needed to reach equilibrium). Another limitation of the usual derivation is the assumption that at $t=0$, the system may be represented by an ensemble whose density matrix is diagonal in the representation corresponding to the eigenstates of the unperturbed system. Van Kampen presents a more general treatment, avoiding the use of the perturbation method and the special assumptions about the initial state. The main problem is to understand why it is permissible to discard cross-products of different probability amplitudes. He discusses first the most appropriate

definition of phase cells [see also von Neumann (55)]. The existence of these phase cells is predicated upon the supposition that one measures slowly varying operators, a condition expressed mathematically

$$\Delta A \gg \dot{A}\Delta t \qquad 12.$$

where ΔA is the error in the measurement of an operator A and Δt is the duration of the measurement. The condition of slow variation of all measured quantities implies that quantum uncertainties are negligible in comparison with experimental error. This condition allows one to form a complete set of commuting operators from the original noncommuting set. The members of the set can now be diagonalized, and the diagonal form divided into blocks. In each block all the terms are equal. The diagonal length of the block is of the order of experimental error of the operator. A set of blocks is called a phase cell and is labeled with the multiple index J. Hence, each phase cell consists of a large number of different quantum states. It is assumed that owing to the large number of randomly varying phases of probability amplitudes belonging to a cell, only the squared terms survive. This assumption of initial randomness is weaker than the usual one.

The average value of a coarse-grained operator is

$$A_r = \sum A_{rJ} P_J$$

where P_J is the probability that the system is in cell J and A_{rJ} the value of A_r in J. Therefore, the expectation of a macroscopic quantity in a pure quantum state is found as the average of that quantity over a certain classical ensemble (characterized by the probabilities P_J).

Van Kampen then studies the time-dependence of the P_J merely by using the time displacement operator $\exp(iHt)$ and the assumption of randomness of phases. This permits him to write the set of equations

$$P_J(t) = \sum_{J'} [J \mid J']_t P_{J'}(0) \qquad 13.$$

which he transforms into

$$\dot{P}_J = \sum_{J'} W_{JJ'} P_{J'} \qquad 14.$$

These equations are of the required form with transition probabilities $W_{JJ'}$. However, Van Kampen does not really justify the passage from (13) to (14). Even the existence of the time-independent transition probabilities seems not proven to the reviewer.

It is quite easy to show that $[J \mid J']_t$ has the required symmetry properties to give the Onsager relations including the case of a magnetic field. Van Kampen has asserted that the Onsager relations in the presence of a magnetic field ($L_{ij}(\mathcal{H}) = L_{ji}(-\mathcal{H})$) may not be demonstrated in the framework of the Pauli perturbation technique. As the method of Pauli does not destroy the time symmetry of the quantum mechanical equations of motion, there is no reason why this should be so. Indeed, the converse is readily demonstrated.

In the presence of a magnetic field application of the Dirac perturbation

technique gives for the transition probability due to a perturbation V

$$P_{nm} \sim \langle n | V_s^z | m \rangle \langle m | \overline{V}_s^z | n \rangle$$

where

$$V_s^z = e^{-iH_0(\mathfrak{IC})t/\hbar} V e^{iH_0(\mathfrak{IC})t/\hbar}$$

$$\overline{V}_s^z = e^{-iH_0(-\mathfrak{IC})t/\hbar} \overline{V} e^{iH_0(-\mathfrak{IC})t/\hbar}$$

H_0 = zeroth order Hamiltonian considered to contain the magnetic field $\mathfrak{IC}$; i.e., one matrix element is calculated on the basis of a zeroth order Hamiltonian with $+\mathfrak{IC}$, whereas its complex conjugate contains $-\mathfrak{IC}$. Reversal of indices then requires reversal of $\mathfrak{IC}$ to ensure symmetry.

The main result of Van Kampen's paper is the demonstration that the elements of a slowly varying operator in the energy representation decrease with increasing distance from the diagonal. This permits one to think that the initial randomness of phases will not be destroyed over a rather long period.

Green (56, 57) has written a paper continuing his previous work on the statistical mechanical theory of irreversibility using the framework of Markoff random processes. He defines his "gross" variables in a Fourier space and traces their equations of motion. It is shown that irreversible behavior arises from statistical correlations evolving in the Markoff process. The theory gives the phenomenological equations of Navier-Stokes and energy balance, but with no clear cut recipe for the calculation of the phenomenological coefficients except in the case of dilute gases, where one recovers the Chapman-Enskog results.

Zwanzig *et al.* (58) have cast Kirkwood's Brownian motion formalism of pure liquids (59) into a form convenient for calculation of the heat conductivity of liquids. Employing the theoretical equilibrium distribution for argon, they have obtained a value of the heat conductivity in good agreement with experiment.

Ross & Kirkwood (60) have presented a proof of the Uhling-Uhlenbeck quantum generalization of the Maxwell-Boltzmann transport equation. They integrate down the Wigner function analogue of the Liouville equation to the singlet space. Then by use of Kirkwood's time smoothing approach (successful in the classical case), coupled with the Born collision approximation, the surmised equation of Uhling and Uhlenbeck is derived.

Finally, we wish to mention papers by Frisch (61) and Fano (62). Frisch has considered the system of equations for the multiple distribution functions and presents a method of successive iterations. His method is somewhat similar to that of Bogolioubov & Gourov (63, 64). Fano presents a generalization of the perturbation method of Callen (65, 66) and co-workers in which a small system is coupled to a large dissipation system.

Some Equilibrium Properties

Condensation.—The problem of condensation of imperfect gases continues to attract much interest. Clearly the condensation phenomenon

depends on the asymptotic behavior of the virial coefficients, B_m, as $m \to \infty$. An important contribution to this problem has been published by Riddell & Uhlenbeck (67). They have solved the underlying combinatorial problem which is the determination of the number of certain types of connected graphs of l points and k lines ("stars"). This problem is independent of any assumption about intermolecular forces. On the other hand, the problem of evaluating the corresponding integrals over functions of the intermolecular potential is far from being solved. We do not think that it is possible to summarize in a few lines here the rather involved arguments of Riddell and Uhlenbeck.

Berlin, Witten & Gersch (68) have approximated the partition function of the classical imperfect gases by a cell model in which the number of particles in a cell is taken as the statistical variable. After some approximations the potential energy may be written as a quadratic form of these cell occupation numbers. The interesting feature of their paper is that isotherms present a critical temperture, and below this temperature they are nonanalytical functions of v consisting of three pieces. Unfortunately, the condensation pressure is not constant. This paper presents a relatively simple mathematical model which reproduces one of the most characteristic aspects of real condensation.

The consideration of the cell occupation number as a variable is also characteristic of Siegert's (69) approach. He uses a subdivision of the total volume V into n equal cells each containing a number of molecules sufficiently large so that interactions between cells become small in comparison with the interactions within each cell. This model has been used previously by Van Hove (70) to obtain interesting information about the behavior of the pressure in the region of condensation. Neglecting completely the interactions between the large cells, Van Hove has shown that the pressure is a nonincreasing function of V/N in the limit $N \to \infty$ and $V \to \infty$ (V/N finite). The mechanical condition of stability ($-\partial p/\partial v \geq 0$) is automatically satisfied in canonical ensembles. Isotherms with unstable regions ($-\partial p/\partial v < 0$) can only result from approximations in the evaluation of the partition function. Katsura & Fujita (71) have tried to use such a model for the condensation process. They assume that the probability of finding n particles in a cell has two sharp maxima, n_1 and n_2. Again neglecting the interaction between the cells, one obtains immediately the pressure and the density of the total system. The density really increases from n_1 to n_2 over a very small region of pressure. However, both the density and the pressure are analytic functions of the fugacity, a situation which does not correspond to the definition of a phase transition.

Siegert has improved Katsura's and Fujita's theory by taking account of the interaction between adjacent cells. By use of the assumption that there exist two sharp maxima for the occupation numbers, the grand partition function is readily transformed into a form equivalent to the three dimensional Ising model, for which there exist approximate calculations.

Siegert shows that the interaction energy required to change the con-

tinuous increase of the density obtained by Katsura & Fujita into an actual discontinuity is indeed extremely small.

An interesting discussion of condensation has been published by Ikeda (72). His method is based on an approximate subdivision of the clusters into "small" and "large" clusters. It permits consideration of the volume dependence of the large clusters.

Katsura (73) has discussed the partition function of the Ising lattice which has a small number of lattice points.

Finally we may briefly mention a paper by Temperley (74). Temperley tries to test Mayer's theory of condensation against a simple model of an imperfect gas. He considers short-range repulsive forces and long-range weak attractive forces. The repulsive forces are taken account of in an approximate way by dividing the volume V into N compartments and neglecting cell configurations with more than 1 particle per compartment. He shows the importance of the order in which the two relevant limiting processes are carried out (number of molecules $\to \infty$, $V \to \infty$). This point has, however, been already emphasized by Katsura & Fujita (75) [see also Kahn & Uhlenbeck (76)].

Monte Carlo method.—The mathematical difficulties in the evaluation of partition functions for interacting particles are so enormous that there exists at present no satisfactory theory for dense systems. For this reason, numerical calculations of statistical properties by high-speed machines are of great importance. Of particular significance is the work published by Rosenbluth and Rosenbluth for three-dimensional hard spheres (77). This paper follows a previous publication by Metropolis *et al.* (78). It also contains some qualitative results for a system of two-dimensional molecules with Lennard-Jones interaction. The authors use the Monte Carlo method discussed in detail in the reference (78). Most of the work on three-dimensional rigid spheres was done with a sample of 256 molecules. At each density the radial distribution was obtained and from it, the equation of state, by the virial theorem.

At low densities the equation of state agrees with the virial expression as expected. At high densities it agrees with the simple free-volume theory or cell model.[3] On the contrary, the results at high densities disagree with the superposition approximation of Kirkwood (79, 80); this is in agreement with conclusions obtained by Nijboer & Van Hove (81) and by Nijboer & Fieschi (82) in their calculation of the fourth virial coefficient of hard spheres as well as the corresponding radial distribution function. For this reason as well as its simplicity, the free volume method seems to be at present the most promising approach for liquids. Two other results obtained by the Rosenbluths are interesting. The distribution functions at high densities and at low densities differ by the sign of the curvature at the origin. For $v/v_0 < 1.5$ (v_0 volume per molecule at the closest possible packing) this curvature is positive but for higher values it becomes negative. This transition between the "solid" and "liquid" type distribution functions seems to occur fairly gradually.

[3] For a detailed account of this model see Hirschfelder *et al.* (2, Chap. IV).

There are also some indications that some higher virial coefficients (higher than the fifth) may be negative. This would be quite unexpected for hard spheres.

Cell-cluster model for the liquid state.—The numerical calculations to which we just have referred greatly increase our confidence in the simple free volume or cell method for the description of the liquid state. Lennard-Jones & Devonshire (83) have given a version of this method which expresses, in terms of the intermolecular forces, the partition function corresponding to the motion of a molecule in its cell.

The analysis of experimental data[3] (84) shows that one of the main defects of this model is that the entropy of the liquid is about 2 or 3 cal./mole too small. This is clearly due to the fact that the model retains only that configuration which corresponds to one molecule per cell, hence giving an insufficient description of the disordered motion of the molecules in the liquid state. This method has been improved by many authors by taking account of "holes," that is, nonoccupied cells [Cernuschi & Eyring (85); Ono (86); Peek & Hill (87); and Rowlinson & Curtiss (88)]. This improvement takes account of the existence of other configurations besides the average one (one particle per cell) and increases the entropy. It is, however, powerless to deal with a second defect of the cell model. All molecules make independent motions and the model is a typical one-particle model. Related to this is the fact that it is impossible to introduce quantum mechanical exchange effects which play an important role in quantum liquids like helium. Moreover critical fluctuations will always be too small.

What is clearly needed is a method to go gradually from the one-body cell method to the description of collective motions. A first step in this direction is the introduction of multiply-occupied cells by Janssens & Prigogine (89) and by Pople (90). We may also mention an interesting paper by Harasima (91) who developed a cell model in which two neighboring molecules, interacting one with the other, are assumed to be in the mean field of the others. This model has been used by Harasima to calculate the temperature dependence of the first peak of the molecular distribution function. Such extensions permit one to consider density fluctuations on a molecular scale which play a role at smaller densities where a double or multiple occupation becomes possible. We shall come back in a subsequent section to the application of this method of multiple-cell occupations to liquid helium.

In an important paper de Boer (92) has generalized the cell model of Lennard-Jones in a systematic way by considering the motion of two or more neighboring molecules in a "cell-cluster" of two or more neighboring cells shared collectively by the molecules. De Boer's method follows closely Mayer's theory of imperfect gases. It is possible to define a set of partial probabilities of l molecules in a cell cluster of l cells

$$W_\alpha(\mathbf{r}_1),\ W_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \cdots,\ W_{\alpha \ldots \lambda}(\mathbf{r}_1, \cdots \mathbf{r}_l) \qquad 15.$$

which, for very large clusters, approach the exact probability distribution for the whole liquid which should be introduced into the partition function.

The partial probabilities may be expressed in terms of sums and differ-

ences of products of V functions ($V_\alpha(\mathbf{r}_1)$, $V_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \cdots$) defined as in the theory of imperfect gases (1, 2). These V-functions have the striking property of being zero if at least one of the molecules is placed on one of the lattice positions.

We may introduce the cell-cluster integrals

$$v_{lk} = \frac{1}{l!'}\int V_l(\mathbf{r}_1, \cdots \mathbf{r}_l)d\mathbf{r}_1 \cdots d\mathbf{r}_l \qquad 16.$$

The index k characterizes the type (i.e., geometrical configuration) of cell cluster l.

When the density is high only v_1 will be appreciable, whereas the other cluster integrals will be the smaller the higher the value of l.

Finally, the partition function may be expressed in terms of the v_{lk}. The result is

$$Q_N = \sum_{\{m_{lk}\}}{}' g(m_{lk}) \prod_{l,k} v_{lk}^{m_{lk}} \qquad 17.$$

where $g(m_{lk})$ is the total number of ways in which the N cells can be divided in m_1 cell clusters of 1, $\cdots$ m_{lk} clusters l of type k the whole set being $\{m_{lk}\}$.

The result (eq. 17) is also valid in quantum mechanics. The interest of de Boer's theory lies mainly in its systematic approach to collective motions starting from the one-particle cell model. The difficulty is to evaluate in practice the successive approximations. From the physical point of view, the results should be similar to those of Janssens & Prigogine (89), and Pople (90).

We may also mention here that the cell model proved remarkably successful in dealing with the excess properties of multicomponent systems (cf. below).

Vibration-spectrum of perturbed lattices and isotopic mixtures.—The theory of vibrations of perfect crystals has now attained a state which may be improved in detail only, i.e., a more elaborate evaluation of the frequency distribution of special crystal lattices [see De Launay (93), Garland & Jura (94)]. We wish, however, to mention the interesting paper by Stockmayer & Hecht (95) on the heat capacity of chain polymeric crystals, and the excellent review article by Montroll (96).

At the present time, much research is done in the field of imperfect crystals, and in this problem several methods of approach are followed. The imperfections may be due to lattice defects such as the absence of particles at some points of the lattice, to the presence of several kinds of molecules distributed at random, or to order-disorder phenomena. The theory of imperfect crystals is applicable to a variety of problems, e.g., mixtures of light isotopes at very low temperatures, properties of glasses, semiconductors and alloys, theory of melting, excess properties of solid mixtures, etc.

An interesting paper on the dynamics of disordered chains of harmonic oscillators, with nearest neighbor interaction only, has been published by Dyson (97). The masses of various molecules and the strength of each

coupling are considered to be random variables with known distribution functions. This model does not apply to three-dimensional crystals, although it may be useful for the study of thermal properties of glasses and perhaps also for isotopic mixtures at very low temperatures. The most interesting feature in Dyson's method of approach is the absence of any perturbation calculus. The equations of motion

$$m_j\ddot{x}_j = K_j(x_{j+1} - x_j) + K_{j-1}(x_{j-1} - x_j) \qquad 18.$$

become, by introducing new appropriate variables,

$$\dot{u}_n = \lambda_n^{1/2}u_{n+1} - \lambda_{n-1}^{1/2}u_{n-1} \qquad 19.$$

where the λ's are random variables subject to the distribution functions $G(\lambda_n)$. To determine the frequency spectrum, one has to calculate an intermediate random function $\zeta(a)$ defined by the following continued fraction:

$$\zeta(a) = x\lambda_a/(1 + x\lambda_{a+1}/(1 + x\lambda_{a+2}/(\cdots = x\lambda_a/[1 + \zeta(a+1)] \qquad 20.$$

and to solve an integral equation, which expresses the equality of the probability distributions of the left and right hand sides of 20.

$$F(\zeta) = \int_0^\infty F(\zeta')G[\zeta(1 + \zeta')/x][(1 + \zeta')/x]d\zeta' \qquad 21.$$

Unfortunately, the resolution of (eq. 21) is, in most cases, very complicated, except in the special case of a chain composed of two kinds of atoms distributed at random, the spring constants K_j being fixed and equal. The integral equation then becomes a difference equation which can be solved by an iteration process.

For a special type of probability distribution $G(\lambda)$, given by the author as an illustration, the frequency spectrum can be calculated analytically. It is characterized by two main features: there is a much greater proportion of very low normal frequencies than in the case of a uniform chain, and there is no longer a maximum frequency, owing to the absence of well-defined masses and spring constants. The application of such kind of calculations to the theory of impurity bands with randomly distributed centers, has been briefly discussed by Aigrain (98).

An interesting paper on imperfect crystals dynamics has been published by Stripp & Kirkwood (99) which is devoted to crystal lattices containing Schottky defects (holes). It shows that the influence of such defects on the vibrational part of the partition function increases in relative importance with temperature until kT reaches the value zV (z coordination number, V static binding potential), for which the static and the vibrational part of the partition function become of the same order of magnitude. The relative number of holes is supposed to be small enough to permit calculation of the change of the normal frequencies by a perturbation calculus. The unperturbed system is the perfect crystal, with all its lattice points occupied. The perturbation is composed of two kinds of terms: the terms of the unperturbed system corresponding to the inertia and the potential energy of the molecules which are actually absent, and a term expressing the change in potential energy of a molecule when one or more holes lie in its neighborhood. It is

necessary to take into account the degeneracies of normal modes arising from the crystal symmetry, but this is without influence on the final results, which involve only traces and other invariant combinations of the degenerate submatrices. The first order perturbation contains an independent and constant contribution of each hole; this contribution is somewhat smaller when two holes are first neighbors than when isolated. There are three kinds of second-order perturbation terms: (*a*) self interaction terms equal to about 15 per cent of the first-order terms; (*b*) nearest-neighbor interaction terms; (*c*) terms arising from pairs at large distances, which decrease as R^{-6} and may be neglected in comparison with the nearest-neighbor terms.

The equilibrium hole concentration is found to exceed that for the static model. If the melting of the crystals is considered to be an order-disorder transition due to the growth of holes, the melting temperature calculated according this theory should be halved by including the vibrational terms in the partition function.

About the same conclusion was reached by Saroléa (100) who studied the influence of the changes of volume of the lattice with temperature and the influence of the lattice vibrations. The value of the critical temperature is decreased. It is thus a general feature that the lattice vibrations favor the disappearance of long-range order and lower the critical temperature associated with the order-disorder transition.

The influence of order-disorder phenomena on the zero-point energy of isotope mixtures has been studied by Prigogine, Bingen & Jeener (101, 102) in the case of one-dimensional and three-dimensional crystals. If one considers the following reaction between two isotopes A and B

$$A_2 + B_2 \rightarrow 2AB \qquad 22.$$

the zero-point energy before and after the reaction can be evaluated by means of the classical formula

$$E^\circ = 1/2h\sqrt{k/m_r} \qquad 23.$$

where m_r is the reduced mass. Since $(m_r^{A_2})^{-1/2}+(m_r^{B_2})^{-1/2} < 2(m_r^{AB})^{-1/2}$ the zero-point energy of the r.h.s. is higher than that of the l.h.s. At 0°K., the stable state requires the absence of AB molecules. The same effect may be expected in crystals. To calculate it, the authors suppose a perturbation calculus can be used. The unperturbed system consists of a crystal whose molecules all have the same mass, equal to the mean mass of the isotopes. The masses are treated as random variables. The perturbation acts on the kinetic part of the Hamiltonian and not on the potential as is usually the case. The first-order perturbation has no effect but the second-order perturbation gives an increase of zero-point energy equal to

$$\Delta E^\circ = \gamma(x_A\mu_A^2 + x_B\mu_B^2)E^\circ(\overline{M}) \qquad 24.$$

where γ is a function of the long-range order, $\overline{M}$ the average mass per atom and where μ_A, μ_B are defined by

$$M_A = (1 + \mu_A)\overline{M}$$
$$M_B = (1 + \mu_B)\overline{M}$$

For a body-centered cubic lattice

$$\gamma = 0.379 \text{ for random mixing.}$$

The effect is rather small.

At 0°K., the stable state is always the separation of the two isotopes. This result indicates a quantum-transition independent of any effect of the statistics, which should arise at very low temperature (<0.1°K.). A somewhat similar problem has been considered by Men & Orlov (103). They consider only a one-dimensional lattice with small differences in mass between the two kinds of molecules. The force constant is assumed to be the same for all pairs of molecules. This excludes, in the opinion of the reviewer the application to superlattices [see also Sarolea (98)] and limits it to mixture of isotopes. Men & Orlov show that with an error of $(\Delta M/M)^2$ the frequency spectrum is the same as that of a regular lattice ABAB $\cdots$ with effective masses which depend on the long-range order and the composition of the system.

In the two papers by Prigogine *et al.* we just have reviewed (101, 102), the zero-point energy of isotopic mixtures has been compared with its value for pure isotopes, neglecting anharmonic forces. On the other hand, the paper by Prigogine, Bingen & Bellemans (104) deals with the effects of anharmonic forces. The importance of these forces manifests itself by the wide variation of the molar volume of hydrogen or helium isotopes. To deal with such effects, Prigogine, Bingen & Bellemans introduce the following basic assumption: the free energy of an isotopic mixture is, for given values of volume per particle and temperature, the sum of the free energy of the pure isotopes and a term due to the combinatorial entropy of mixing:

$$f(v, T) = x_A f_A(v, T) + x_B f_B(v, T) - T s_m \qquad 25.$$

$$s_m = k \ln \frac{N!}{N_A! N_B!} \qquad 26.$$

Let us suppose that for given pressure and temperature the molar volumes of the pure isotopes and of the mixture are in the order $v_B < v < v_A$. If, by compression and dilatation we give to the molar volume of both pure isotopes the common value v and then mix them, formula 25 expresses that the only change of the free energy would be the appearance of the term Ts_m due to the combinatorial entropy. This assumption is automatically satisfied in simple statistical models of condensed phases like the cell model or an assembly of anharmonic oscillators, the effect of the localization of masses on the normal frequencies [dealt with in the papers (101, 102)] being not taken into account. This latter effect becomes only dominant for the rather academic case of heavy molecules. Using formula 25, all the thermodynamical properties of an isotopic mixture may be expressed in terms of the properties of the pure isotopes. For example, the excess free energy (that is the free energy of mixing less the contribution due to s_m) becomes

$$f_e = \frac{1}{2} x_A x_B (v_A - v_B)^2 \left(x_A \frac{\partial^2 f_A}{\partial v_A^2} + x_B \frac{\partial^2 f_B}{\partial v_B^2} \right) > 0 \qquad 27.$$

Agreement is reached with the experimental material published up to date on thermodynamic properties of isotopic mixtures (H_2—D_2; H_2—HD; T_2—D_2; He^3—He^4). The present lack of sufficient experimental data prevents the testing of the predictions of the model concerning, for example, change of volume or excess entropy.

The main conclusion is that the excess free energy is always positive so we have to expect phase separation at sufficiently low temperature. The critical temperature of mixing has been estimated to be about 2°K. for solid H_2—D_2 mixtures and 0.7°K. for liquid He^3—He^4 mixtures. This would be a general type of purely quantum phase transition. The positive deviations from Raoult's law met in He^3—He^4 solutions would be a particular case of a general phenomena. Of course, certain effects like the change of the λ point of He^4 with the concentration of He^3 are specific to this mixture and require a generalization of the additivity hypothesis (formula 25) which takes into account the difference in statistics.

A strong support for this view is the fact that the liquid mixture H_2—D_2 studied by Hoge & Arnold (105) (this seems, unfortunately, the only system besides He^3—He^4 whose vapor pressure has been measured) presents an excess free energy which is of the same order of magnitude as for He^3—He^4 mixtures. But as the temperature is much higher, the corresponding deviations from Raoult's law are much smaller.

In his paper on the theory of liquid He^3—He^4 mixtures, Goldstein (106) considers mixtures of an ideal (or almost ideal) Bose-Einstein gas and ideal Fermi-Dirac gas. The model is practically identical with that of Heer & Daunt (107, 108). In contrast to the papers reviewed above, the deviations from the laws of perfect mixtures are described as being due to the difference in statistics. The model exhibits complete miscibility at all temperatures together with a vanishing entropy in all possible mixtures at the approach of the absolute zero.

A detailed discussion of the properties of He^4—He^3 mixtures, based on a phenomenological modification of the theory of Daunt & Heer (107, 108), has been published by Mikusa (109). One may hope that experimental investigations on mixtures of He^3—He^4 (especially the volume effect of mixing and solid mixtures) and of other isotopic mixtures (like H_2—D_2 · · ·) will lead to a clarification of the relative effect upon the thermodynamic properties resulting from difference in masses and difference in statistics.

Miscellaneous.—The interest of finding some cases in which partition functions of interacting many-particle systems may be calculated explicitly, has induced many authors to study in some detail simplified one-dimensional models (110 to 115).

Ramanakrishnan (116) and Ramanakrishnan & Matthews (117) have published some mathematical considerations on one-dimensional systems related to earlier work on the "theory of product densities."

The thermal properties of a linear chain interacting through a Morse potential

$$V = \sum D[\exp\{-a(y_n - y_{n-1})\} - 1]^2$$

have been studied by Dugdale & MacDonald (118).

The behavior of the linear chain changes radically when a critical pressure p_{cr} is crossed—which is a function of the reduced temperature. For $p > p_{cr}$, the system behaves like a condensed phase whereas for $p < p_{cr}$, it has all the properties characteristic of a linear gas (equation of state, etc.). There exists, however, no real phase transitions in these systems.

The statistical mechanics of one-dimensional multicomponent systems with nearest neighbor interactions has been developed by Prigogine & Lafleur (119). The purpose of this paper was to test the statistical mechanical theory of solutions based on the cell model which has been put forward by Prigogine and his co-workers (120 to 123). The conclusions, mainly concerning the origin of the excess thermodynamic functions (excess free energy, excess volume) agree with those deduced from the cell model.

The relations between successive multiple distribution functions (partially integrated forms of Liouville's theorem) play a central role in the work of Born-Green, Kirkwood, and others. Lion (124) has established some new recurrence relations between these distribution functions, but their complicated form makes it unlikely that they may be used as a starting point for new methods of evaluation of statistical quantities.

Münster (125) discusses the relation between the different statistical ensembles. They are related by Laplace-transforms. The corresponding stability conditions are stated.

An interesting experimental and theoretical study of critical opalescence in mixtures has been presented by Fürth & Williams (126), and Quantie (127). Two classes of mixtures have been examined. In one class the refractive indices differ considerably, in the other, but slightly. Light scattering in mixtures of critical composition is measured as a function of angle. Near the critical temperature strong angular dependence of the scattering is found, indicating large deviations from the Rayleigh scattering law. The authors account for these deviations by supposing them to result from large fluctuations in composition near the critical temperature. Assuming that fluctuations in composition are independent of the total density fluctuations, one may interpret the scattering distribution as the Fourier transform of the composition fluctuations as a function of distance. By Fourier inversion of the data one finds $\delta c(\mathbf{r}_1)\delta c(\mathbf{r}_1+\mathbf{r})$ as a function of $\mathbf{r}$. This distribution is Gaussian except in some special cases for large $\mathbf{r}$. In all cases, the range of correlation increases with the approach to the critical temperature where it is of the order of 1000 Å. On this basis, the authors state that the rather heterogeneous state of a mixture immediately above its critical point requires a "readjustment" of our phenomenological ideas of phase transitions in the critical region.

Finally we wish to mention the interesting papers by Pople (128) on axially symmetric molecules.

Liquid Helium

Before going into the discussion of some recent papers on liquid helium we wish to call attention to the excellent review article by Daunt & Smith (129) in which an extensive bibliography may be found.

The most characteristic feature of helium is probably the large value of the so-called "reduced" de Broglie wave length (130).

$$\Lambda^* = \frac{h}{\sigma\sqrt{m\epsilon}} \qquad 28.$$

where σ, ϵ are the characteristic parameters in the "6–12" interaction law. The quantity Λ^* is 2.64 for He^4 and 3.04 for He^3 which may be compared with 0.591 for Ne and 1.73 for H_2. The quantum zero-point energy is then of the same order as the energy of the intermolecular forces, and heat of vaporization of liquid helium is smaller than that of a classical liquid (by an order of magnitude).

The usual approach, due to London (131), is to start with a perfect Bose-Einstein case to describe the porperties of He^4. This model, even with minor refinements (132, 133), does not consider the mutual interactions between the helium atoms in a correct way.

The experimental data, mainly on the specific heat of He^4 [Kramers, Wasscher & Gorter (134)] and He^3 [Abraham *et al.* (135); Sydoriak & Roberts (136); de Vries & Daunt (137)] clearly show the failure of any ideal gas model. The same conclusion follows also from the data on magnetic succeptibility [Fairbank *et al.* (138, 139)].

A well-known method due to Landau (140) permits one to avoid, in a certain sense, these difficulties by going directly into a quantum description of a continuous medium. This method has been improved and extended recently by Thellung (141) and Ziman (142), and Penrose (143) has used it in a general paper concerning the quantization of sound waves. In spite of the great value of this approach, it does not permit one to understand the special features of He^4 from first principles, because it avoids an atomic description. A satisfactory theory must be founded on assumptions about the interactions between molecules, their masses, and their statistics.

The problem of the influence of the interactions may be approached from different directions. Many authors [Green (144); Goldberger & Adams (145); and Siegert (146)] have considered the expansion of the quantum mechanical partition function in powers of the interaction potential. In a very interesting paper, Chester (147) has demonstrated a simple method for this expansion. His series are valid for all types of statistics and for all types of interactions, provided the intermolecular potential has no singularity. He shows, however, that his expansion remains valid if the particles are assumed to have finite incompressible cores, but in this case the terms of the series depend on the matrix elements involving the wave functions of the corresponding "hard sphere" problem. We may also mention briefly at this point, the perturbation methods for the expansion of the quantum mechanical partition func-

tion based on the number representation published by Ichimura (148) and Mac Donald & Richardson (149).

In a subsequent paper, Chester (150) applies his results to the problem of liquid helium. He considers mainly the λ transition. He argues that as the volume of the incompressible core is much smaller than the mean volume per particle, it is reasonable to replace the wave functions of the hard sphere problem by the suitable wave function of the perfect Bose-Einstein gas. The first term of the "approximate" expansion of the partition functions is thus a perfect Bose-Einstein partition function and leads to a third-order transition. The second term can be easily calculated in the same way. It is shown to give rise to a transition of the second-order. Thus, Chester has succeeded in proving that even small attractive forces change the nature of the λ-transition. This is a very interesting result and Chester's theory is a definite improvement over London's original model. However, the suppression of the short-range repulsive forces does not seem to be justified because certainly these forces play an important role in the origin of the large zero-point energy of liquid helium and in the occurrence of phonons at sufficiently low temperatures.

The point of view developed by Prigogine & Philippot (151) is summarized in a paper by Prigogine (152). It is a remarkable fact that the thermodynamic properties (volume, heat of vaporization) at absolute zero seem to be largely independent of statistics. The physical picture underlying this model is then the following: At 0°K. we have a more or less regular distribution of particles in which each atom tends to remain separate from the others. This arises by compensation of effects of intermolecular forces and curvature of the wave functions. This state is mainly statistics-independent. Statistics, however, plays a leading role in the excitations. When we raise the temperature we first have to consider the formation of phonons. But, in addition, because of the large spacing between molecules, a kind of order-disorder process is possible which corresponds to density fluctuations on a molecular scale. It may easily be shown that the excitation energy of this process depends strongly on the statistics. In the case of He^4 it gives rise to a large supplementary specific heat with a λ transition. This description remains largely qualitative. However, the quantitative calculations give correct orders of magnitude. The interesting feature of this simple model is that it provides us with excitations which are directly related to the particular nature of He^4, that is, to the large value of the reduced de Broglie wave length Λ^* and to its statistics. Moreover, it gives a means for relating different characteristically striking properties like the decrease of the molar volume with increasing temperature below the point and the anomalous specific heat.

We shall now consider Feynman's stimulating contribution to the theory on liquid helium (153, 154, 155). This author presents an expression for the quantum mechanical partition function based on his Space-Time approach to nonrelativistic Quantum Mechanics (156). This approach is mathematically equivalent to the usual formulation but emphasizes many interesting as-

pects of quantum mechanics which are not so clear in the other formulations [cf. the excellent review article by Montroll (157)].

Feynman (151) shows that the wave function at time $t+\epsilon$ may be expressed in terms of its value at time t in terms of

$$\Psi(x, t+\epsilon) = \int \Psi(\lambda_0, t) K(x, x_0; \epsilon) dx_0 \qquad 29.$$

where the kernel K is proportional to the exponential of the classical action integral (time integral of the Lagrange function). From this, one obtains in a way somewhat similar to that used in the theory of Markoff processes

$$\Psi(x, y) = \lim_{n\to\infty} \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \Psi(x_0, 0) K\left(x_1, x_0; \frac{t}{n}\right) K\left(x_2, x_1; \frac{t}{n}\right) \cdots K\left(x, x_{n-1}; \frac{t}{n}\right) dx_0 dx_1 \cdots dx_{n-1} \qquad 30.$$

This method may be used to express matrix elements in terms of such function space integrals, and hence the quantum partition function which is the trace of the operator $\exp(-\beta H)$ where $\beta = 1/kT$. Feynman then argues that the effect of the other atoms in liquid helium is not to offer a potential barrier (because every atom in its motion may "push" aside the other atoms) but a kind of kinetic barrier changing only the effective mass from m to m'. The quantum partition function becomes then proportional to

$$\sim \int \sum_P \exp - \frac{m'}{2\beta\hbar^2} \sum_i (\mathbf{r}_i - P\mathbf{r}_i)^2 \times \rho(\mathbf{r}_1, \mathbf{r}_2 \cdots, \mathbf{r}_N) d\mathbf{r}^N \qquad 31.$$

This expression differs from that for a perfect Bose-Einstein gas (1, 158) only in the factor $\rho(\mathbf{r}_1, \cdots \mathbf{r}_N)$ which is mainly introduced to avoid overlapping of particles.

Interesting comments on this point of Feynman's paper have been published by Chester (159) and ter Haar (160). A practically identical expression to eq. 31 may be readily deduced by the usual methods if one introduces the approximation

$$\exp(-\beta H) = \exp(-\beta V) \exp(-\beta T) \qquad 32.$$

that is, one neglects the commutator of potential and kinetic energy. The inclusion of the commutator would involve a power series in $\hbar$. Unfortunately, at the present the error involved in equations 31 or 32 is very difficult to estimate and for this reason 31 has only a semiempirical character. By a rough analysis of 31, Feynman deduces the existence of a third-order transition.

Chester (159) and Temperley (161) discussed the approximations involved and Chester (159) stressed the similarity of Feynman's method with that developed earlier by Matsubara (162). Using a rough approximation for ρ (cf. eq. 31) which supposes that the particles are located on a simple cubic lattice, Kikuchi (163) obtained a second-order transition. The detailed discussion of the order of the transition based on eq. 31 seems, however, somewhat premature.

In his second paper, Feynman (154) discusses the nature of the excita-

tions of liquid helium at very low temperatures ($<0.5°$K.). Longitudinal phonons represent a possible mode of excitation with a very low energy of excitation. The existence of phonons can be made plausible as argued by Feynman, from a microscopic point of view. However, a rigorous proof for their existence is yet lacking except for nearly trivial cases (i.e., hard spheres on a line, Philippot (164)].

Feynman insists on the importance of the Bose-Einstein statistics in the discussion of other possible states of low energy. For Boltzman statistics, exchange of atoms is a new state, but not for Bose-Einstein statistics. Some possibilities which might at first be thought to exist, like the rotation of a large ring, are shown to correspond in reality to a high excitation energy. So Feynman makes it plausible that no states close to the ground state exist, exclusive of phonons.

However, Feynman does not succeed in making precise the nature of the lowest excited state (excluding phonons). There may be a small rotating ring of atoms, or the rapid motion of an atom, or the excitation of an atom in its cell [we may add here probably the density fluctuations on a molecular scale referred to above (152)].

Finally, in his third paper (155), Feynman discusses the form of the wave function representing an excitation in liquid helium. He gives arguments that for the excitations he has considered in his paper II, this function is of the form

$$\phi \sum_i f(\mathbf{r}_i) \qquad 33.$$

where ϕ is the ground state wave function, $f(\mathbf{r})$ some function of the position and the sum is taken over all atoms. For example, to an individual excitation of the form $\phi \exp. i\mathbf{k}\cdot\mathbf{r}$ corresponds the symmetrical sum $\phi \sum_i \exp i\mathbf{k}_i\mathbf{r}_i$ which is of form 31. The best form of the function $f(\mathbf{r})$ is easily determined by a variational principle. An interesting result obtained by Feynman is that the "best choice" corresponds to

$$\phi \sum_i \exp i\mathbf{k}_i \cdot \mathbf{r}_i \qquad 34.$$

This form of the wave function has been suggested a long time ago by Bijl (165). For a given value of k the energy is lower for eq. 34 than for any other functions. This energy is

$$E(\mathbf{k}) = \frac{\hbar^2 k^2}{2mS(\mathbf{k})} \qquad 35.$$

where $S(\mathbf{k})$ is the Fourier transform of the radial distribution function. Using the experimental data on $S(\mathbf{k})$, Feynman obtains an energy spectrum which qualitatively corresponds to Landau's form with a minimum. Excitations near the minimum behaves like Landau's rotons.

This result by Feynman is certainly an important step toward the molecular understanding of the Two-Fluid model of liquid helium. The discussion of this model by Feynman is outside the scope of this review article. We wish, however, to emphasize that the atomic nature of the excitations still remains uncertain.

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